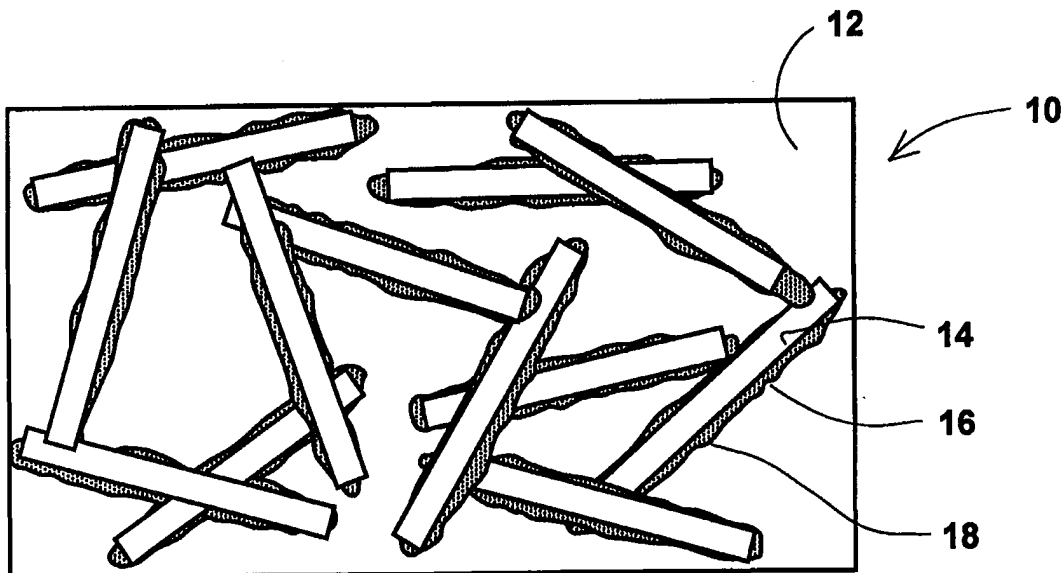




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<p>(21) International Application Number: PCT/IL97/00342 (22) International Filing Date: 26 October 1997 (26.10.97) (30) Priority Data: 60/030,621 7 November 1996 (07.11.96) US (71) Applicant: CARMEL OLEFINS LTD. [IL/IL]; P.O. Box 1468, 31014 Haifa (IL). (72) Inventors: NARKIS, Moshe; Lavon Street 3, 34951 Haifa (IL). TCHOUDAKOV, Rosa; Aba Hillel Silver Street 29/14, 32693 Haifa (IL). SIEGMANN, Arnon; Amnon veTamar Street 6, 32545 Haifa (IL). VAXMAN, Anita; Handke Street 64, 34608 Haifa (IL). (74) Agent: A. TALLY EITAN-ZEEV PEARL, D. LATZER & CO.; Lumir House, Maskit Street 22, 46733 Herzelia (IL).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: ELECTRICALLY CONDUCTIVE COMPOSITIONS AND METHODS FOR PRODUCING SAME



(57) Abstract

An electrically conductive composition (10) and a method for producing same, for example by injection molding. The composition includes a matrix comprising substantially a first thermoplastic component (12), a second thermoplastic component (16) having a higher polarity than that of the first thermoplastic component, the second thermoplastic component encapsulating a plurality of fibers (14) forming a network of encapsulated fibers within the matrix, and a carbon component (18) preferentially attracted to the second component so as to make said network and electrically conductive network within the matrix.

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ELECTRICALLY CONDUCTIVE COMPOSITIONS AND METHODS FOR PRODUCING SAME

FIELD OF THE INVENTION

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The present invention relates to electrically conductive composites based on a mixture of two thermoplastic compounds having different polarity with glass fibers and carbon black and or carbon fibers and to methods for producing same.

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BACKGROUND OF THE INVENTION

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Electrically conductive polymer based compositions are used in many industrial applications, such as for dissipating electrostatic charge from plastic parts and plastic boxes for shielding electronic components from electromagnetic interference (EMI). Examples for electrostatic discharge (ESD) applications are electronic packaging, clean room installations, storage trays, water carriers, chip carriers and construction components for explosion-proof environments.

20

Compounds tailored for dissipating static electricity having a typical surface resistivity of 10^2 to 10^{13} ohm/square and compounds specified for EMI shielding applications typically exhibit volume resistivity of 10^{-2} to 10^2 ohm-cm.

25

There are known in the art polymer based compounds having appropriate resistivity for both static electricity dissipation and EMI shielding. One class of compounds known in the art is based on polypropylene (PP) or polyethylene (PE) with high carbon loading levels up to 40 to 60% by weight characterized by surface resistivity of about 10^3 - 10^8 ohm/square. For applications requiring EMI shielding, weight loading levels of 30 to 50 % PAN carbon fibers, 40 % aluminum flakes, 15 % nickel-coated carbon fibers or 5 to 10 % stainless steel fibers have been used for the same class of polymers.

30

The method currently used to increase the electrical conductivity of polymers is to fill them with specific conductive additives, such as metallic powders, metallic fibers, carbon black, carbon fibers and recently by intrinsically conductive

polymeric powders. The characteristic behavior of these materials is the existence of a strongly non-linear relationship between the electrical conductivity and the filler concentration. At low filler loading, the electrical conductivity of the polymeric compound is generally quite low; its magnitude is similar to that of the polymer matrix (10⁻¹⁶ to 10⁻¹¹ ohm⁻¹ cm⁻¹). As loading is increased, the conductivity increases sharply by several orders of magnitude over a narrow concentration range, then slowly increases towards the conductivity of the condensed filler powder of the order of 10⁻⁴ to 10⁻¹ ohm⁻¹cm⁻¹. This behavior describes an insulator-conductor transition occurring at a critical volume fraction (percolation threshold). This threshold is due to the formation of a chain-like network of particles extending throughout the entire specimen volume and allowing electrical current to flow.

US Patent No. 4,169,816 describes an electrically conductive single thermoplastic material composition with a high carbon content, the composition including for each 100 parts of polypropylene-ethylene copolymer 15 - 30 parts of carbon black, 0.25 to 1 part of silica and 1 - 10 parts of a fiber reinforcing agent selected from carbon fibers or a mixture of carbon fibers and glass fibers.

US Patent No. 5,004,561 describes another single thermoplastic based electrically conductive composition with a high carbon content, the composition including for each 100 parts of thermoplastic resin selected from the group of polyolefin, polystyrene and acrylonitrile/styrene/butadiene (ABS) copolymer resin, polybutylene terephthalate (PBT) resin, polyphenylene ether and polyamide (PA) resin, 30 - 300 parts of electrically conductive glass fibers, 5 - 40 parts of carbon black and 5 - 40 parts of graphite.

Russian Patent No. SU 1,643,568 describes a high carbon based electrical conductive thermoplastic composition in which electrical conductivity is achieved from the dispersion of carbon in the matrix. The composition includes 20-35 weight percent polypropylene, 10-20 weight percent polyamide, 20-30 weight percent carbon black, 10-20 weight percent graphite and 15-20 percent glass fibers.

There are generally two methods for producing electrically conductive thermoplastic articles known in the art. In the slow production rate compression molding method less filler (e.g. carbon black) is required to achieve a desired conductivity,

however the mechanical properties of the composition are usually deficient. In the fast production rate injection molding method better mechanical properties are achieved and articles having complex geometry can be produced but the amount of conductive filler required is high. One deficiency of compression molding of electrically conductive compounds is that the relatively slow processing is expensive.

A major disadvantage of prior art polymer based compounds for electrostatic dissipation and EMI shielding applications is the high percentage of conductive additives required to form the conductive polymer compounds resulting in high cost and deficient processability and mechanical properties and also high carbon contamination which is adverse in particular for clean room applications.

SUMMARY OF THE INVENTION

The present invention provides an improved thermoplastic electrically conductive composition.

5 According to an aspect of the present invention, the electrically conductive composition includes a first thermoplastic component forming a continuous matrix and a second thermoplastic component having a polarity larger than the polarity of the matrix. The composition also includes fibers being encapsulated in-situ by the second thermoplastic component and forming a network within the matrix and also a
10 carbon black component which is preferentially attracted to the second component due to its higher polarity. The in-situ formation of an encapsulated network, including carbon black, in preferred locations of particles provides an electrically conductive composition.

 According to a further aspect of the present invention, the ratio between the conductive carbon filler and the second component is sufficiently high so that a
15 substantial part of the carbon filler is located at the interface between the second component and the matrix to provide the electrical conductivity. Nevertheless, the overall concentration of carbon is at least an order of magnitude smaller than in the prior art electrically conductive compositions, thus making the compositions of the present invention advantageous in many applications including clean room applications.

20 Another object of the present invention is to utilize a fast processing method for producing the thermoplastic electrically conductive compositions of the present invention. Injection molding is used for producing the electrically conductive thermoplastic compositions of the recent inventions while using very low carbon black concentrations and improving the mechanical properties of the composition.

25 The electrically conductive composition of the present invention includes a matrix including substantially a first thermoplastic component, a second thermoplastic component having a higher polarity than that of the first thermoplastic component, the second component encapsulating a plurality of fibers forming a network of encapsulated fibers within the matrix, and a carbon component preferentially attracted to the second
30 component so as to make the network an electrically conductive network within the matrix.

In one embodiment of the present invention, the first thermoplastic component is a polyolefin compound with or without an added elastomer component. The polyolefin is selected from the group of polypropylene which may be a homopolymer or a copolymer and polyethylene. The second component is polyamide or EVOH. In a preferred embodiment, the composition includes less than 20 parts per hundred polyamide or EVOH.

In another embodiment, the first component is acrylonitrile/butadiene/styrene and the second component is polyamide, or EVOH.

In yet another embodiment, the first component is selected from polystyrene, high impact polystyrene and polyphenyleneoxide/ polystyrene and the second component is polyamide or EVOH.

The fibers of the compositions of the present invention may be glass fibers. In a preferred embodiment, the composition includes less than 55 parts per hundred glass fibers.

The carbon component of the compositions of the invention of the present invention may be carbon black. Alternatively, or in combination, the carbon component may be carbon fibers. In a preferred embodiment, the composition includes less than 10 parts per hundred carbon black. In another preferred embodiment, the composition includes less than 30 parts per hundred carbon fibers.

In a preferred embodiment, the composition has one or more of a volume resistivity from about 0.1 to about 10^9 ohm-cm, a flexural modulus of up to about 11,000 MPa, and a tensile strength of up to 60 MPa.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be understood and appreciated more fully from the following detailed description taken in conjunction with the appended drawings in which:

5 Fig. 1 is a schematic illustration of the morphology of the electrically conductive thermoplastic compositions of the present invention;

 Figs. 2A-2C are nonlimiting exemplary SEM micrographs (at different magnifications) of freeze fractured surfaces of an injection molded composition of the present invention;

10 Fig. 3 is a schematic block diagram illustration of a method for producing the electrically conductive thermoplastic compositions of the present invention;

 Figs. 4A - 4D are schematic block diagram illustrations of four alternative preferred methods for producing the electrically conductive thermoplastic compositions of the present invention wherein carbon black is the carbon compound; and

15 Figs. 5A - 5C are schematic block diagram illustrations of three alternative preferred methods for producing the electrically conductive thermoplastic compositions of the present invention wherein the carbon compound is both carbon black and carbon fibers.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Reference is now made to Fig. 1. Figure 1 is a schematic illustration of the electrically conductive multi-component thermoplastic compositions of the present invention.

The electrically conductive multi-component thermoplastic composition, generally referenced 10, includes a matrix 12 formed substantially of a first thermoplastic compound, glass fibers 14 encapsulated with a second thermoplastic compound 16 having therein and thereon carbon black shown in the SEM micrographs of Fig. 2. As illustrated in Fig. 1, glass fibers 14 encapsulated with second thermoplastic composition 16 with carbon black thereon form a conductive network within polypropylene matrix 12.

In the preferred embodiments, the first thermoplastic component is a polyolefin based component, polystyrene (PS) based component or acrylonitrile/styrene/butadiene (ABS) terpolymer based compound, with or without an added elastomer component and the second thermoplastic component is polyamide (PA) or Polyethylene Vinyl Alcohol (EVOH) copolymer. Preferably, the elastomer component is a combination of elastomers. The addition of the elastomer component to the compound changes the composition's mechanical properties without significantly affecting its electrical conductivity.

Since the affinity of polyamide or EVOH 16 to glass fibers 14 is much stronger than to any of the first thermoplastic components, during the melt blending of composition 10, the second thermoplastic component preferentially encapsulates, in situ, glass fibers 14 as described in detail with reference to Fig. 3 hereinbelow, thereby producing a network of encapsulated fibers within matrix 12. Moreover, carbon black particles are preferentially attracted to the second thermoplastic component phase and located at the second thermoplastic component (polyamide or EVOH) matrix interfaces as indicated by reference numeral 15, thereby making the network of encapsulated fibers electrically conductive using a much smaller content of carbon black than in the prior art and improving the mechanical properties of composition 10 as described hereinbelow.

Referring to the three Scanning Electron Microscope (SEM) micrographs of Figs. 2A - 2C which differ in their magnification, the network of encapsulated fibers

and the preferential distribution of carbon black 18 in the second thermoplastic component phase 16 is clearly seen.

A particular feature of the present invention is that composition 10 includes much lower concentrations of carbon black than in the prior art for similar levels of electrical conductivities. This is since the electrically conductive carbon black particles form continuous pathways along the interfaces between the second thermoplastic component phase and the matrix (first level of percolation). Moreover, the embedded part of carbon black particles is located within the amorphous phase of the second thermoplastic 16 (second level of percolation), thereby the formation of the conductive pathways is facilitated. This is further facilitated by the network formed of second thermoplastic component encapsulated glass fibers (third level of percolation).

Reference is now made to Figs. 3 through 5C which illustrate preferred methods for producing the electrically conductive thermoplastic compositions of the present invention. Fig. 3 illustrates the method in general and Figs. 4A - 4D and Fig 5A - 5C illustrate, respectively, alternatives of the method for two nonlimiting exemplary compositions.

The method of Fig. 3 illustrated in a time sequence from left to right comprising the steps of compounding 32, the step of pelletizing 34 and the step of injection molding 36. In one preferred embodiment the step of compounding 32 includes the steps of dry blending of polypropylene with second thermoplastic component indicated by reference numeral 31 followed by melting and melt mixing with the glass fibers as indicated by 33 and subsequent melt mixing with carbon fibers, carbon black or both.

In the non limiting examples described below, the compounding step 32 is conducted on a twin-screw compounder (Berstorf, Germany), at processing temperatures in the range of 200-285 °C (corresponding to the melting point of the polymer components) and a screw speed of 55 rpm. The resulting compounds are pelletized (step 34) and then injection molded (step 36) at 200-285 °C on a Battenfeld injection molding machine equipped with a three cavity American Standard Testing Material (ASTM) mold (tensile bar, flexural bar and falling dart impact disc).

Figs. 4A - 4D illustrate four preferred alternatives of the method for producing composition 10 whereas the composition includes carbon black as the carbon

compound. Figs. 4A - 4D are illustrated for the nonlimiting example of a composition 10 comprises 100 parts by weight polypropylene, 12 parts by weight polyamide, 30 parts by weight glass fibers, and 2 parts by weight carbon black.

5 In the embodiment illustrated in Fig. 4A, carbon black concentrate is added in the injection molding stage as indicated by reference numeral 37 rather than in the compounding step 32 resulting in a resistivity of 537 Ohm-cm and flexural modulus of 4819 ± 161 MPa.

10 Fig. 4B illustrates the alternative wherein the carbon black concentrate is dry blended with the polypropylene and polyamide resulting in a resistivity of 432 Ohm-cm and flexural modulus of 4649 ± 32 MPa. Fig. 4C illustrates the alternative wherein the carbon black concentrate is added during compounding resulting in a resistivity of 214 Ohm-cm and flexural modulus of 4491 ± 51 MPa.

15 In the embodiment of Fig. 4D glass fibers are dry blended with the polypropylene and polyamide while carbon black concentrate is added during compounding resulting in a resistivity of 431 Ohm-cm and flexural modulus of 3790 ± 63 MPa.

20 Figs. 5A - 5C illustrate three preferred alternatives of the method for producing composition 10 whereas the composition carbon fibers or carbon black and carbon fibers as the carbon compound. Figs. 5A - 5C are illustrated for the nonlimiting example of a composition 10 comprises 100 parts by weight polypropylene, 12 parts by polyamide, 30 parts by weight glass fibers, and 2 parts by weight carbon black and 20 parts by weight carbon fibers.

25 In the alternative of Fig. 5A both carbon black and carbon fibers are added during the injection molding step resulting in high conductivity (Resistivity of 0.465 Ohm-cm) and high flexural modulus (9770 ± 428 MPa).

30 In the alternative of Fig. 5B carbon black is dry blended with the polyolefin and polyamide as indicated by step 39 instead of the dry blending indicated by step 31 of the other alternatives while carbon fibers are added (step 35) during compounding resulting in a resistivity of 2 Ohm-cm and flexural modulus of 9550 ± 350 MPa.

In the alternative of Fig. 5C, carbon fibers are added in the compounding stage resulting in resistivity of 8 Ohm-cm illustrates and flexural modulus of 8931 ± 267 MPa.

5 It will be appreciated that the specific method used to prepare the compounds forming composition 10 for injection molding can be selected from the non limiting embodiments described hereinabove and from many other variations thereof, thereby varying the specific electrical conductivity and mechanical properties (illustrated by the flexural modulus above) of composition 10. In all methods, the present invention provides an electrically conductive thermoplastic composition which provides high
10 electrical conductivity and strong mechanical properties after injection molding.

The following examples illustrate without limitation certain aspects of the present invention.

In all examples, injection molded composite samples (12.6cm x 1.27cm x 0.32cm) were characterized for electrical properties by measuring volume resistivity,
15 according to ASTM D 257 - 93 and ASTM D 4496 - 87, using Keithley instruments. Silver paint was used to eliminate the contact resistance between samples and electrodes.

The corresponding ASTM test methods were used for the mechanical properties evaluation. Specifically, ASTM D 0638 was used for measuring tensile properties, ASTM D 790 was used for measuring flexure, ASTM D 256 was used to
20 measure IZOD impact and ASTM D 570 was used to measure water absorption.

The glass fiber content and the carbon black content in each specimen was determined by using ASTM D 5630 - 94 and ASTM D 1603 - 94, respectively.

The composites morphology was studied using JEOL 5400 scanning electron microscope. Freeze fractured surfaces were studied.

25 In the experiments, commercial grades of PP (homopolymer and copolymer), ABS, PS, HIPS, NORYL (described in detail with reference to Tables10-13), PE (high and low density grades), elastomer, PA (PA6, PA66, PA 11, PA12, PA 6/6.9, PA 6/12), EVOH, glass fibers (chopped strands, 3.2-6.3 mm length, 10-13 micrometer diameter), conductive carbon black and carbon fibers (chopped fibers,
30 6 mm length, 7-8 microns diameter) have been used in this study. Five types of carbon black were studied. Their properties are shown in Table 1 below.

Table 1

Property	Ketjen EC 300J (AKZO)	Ketjen EC 600JD (AKZO)	Vulcan XC-72 (Cabot)	Corax L6 (Degussa)	Conductex 975 (Columbian Chemicals)
Surface area BET, m ² /g	1000		180	265	250
Particle size, nm	30		29	18	22
Porevolume DBP,ml/100g	350	480	178	123	165
Surface area CTAB, m ² /g	480		86	150	153
Iodine absorption, mg/g	900	1000		293	260
Volatilities, %	0.5	0.6	1.0	1.5	1.0
pH	8	8	7	7.5	7

5 All blend ratios described relate to parts by weight, in each case based on 100 parts by weight of the first compound. An electrically conductive polyolefin composites comprise: 100 parts by weight polymer matrix, 4 to 20 parts by Polyamide, 10 to 55 parts by weight glass fibers, 0.5 to 10 parts by weight carbon black, 0 to 30 parts by weight carbon fibers.

10 The electrical and mechanical behavior of compositions 10 was studied for different polyamide mixtures ratios as a function of glass fiber concentration, polyamide/glass fiber ratio and carbon black concentration. The resistivity and the mechanical properties as a function of composition are summarized in Tables 2A and 2B. It will be appreciated that the samples produced were in accordance with the processing method of the present invention i.e., injection molding.

Table 2A

Composition	1	2	3	4	5
Polypropylene (MFI 12)	100	100	100	100	100
Polyamide 6	5	5	5	5	5
Glass Fiber (Vetro tex)	12	12	20	20	20
Carbon Black (EC 600)	1	3	0.5	1	3
Property					
Flexural Modulus, MPa	3044	3849	3041	3945	4104
Izod Impact, notched, J/m	69	64	33	83	60
Volume Resistivity ohm-cm	$>10^8$	3.3×10^5	10^8	10^4	1.6×10^5

Composition	6	7	8	9	10
Polypropylene (MFI 12)	100	100	100	100	100
Polyamide 6	8	8	10	12	10
Glass Fiber (Vetro tex)	20	30	30	30	30
Carbon Black (EC 600)	3	1	1.5	2	3
Property					
Flexural Modulus, MPa	4366	5003	4655	4941	5153
Izod Impact, notched, J/m	57	76	75	79	65
Volume Resistivity ohm-cm	8.6×10^3	6.6×10^3	3×10^3	1.4×10^3	6.5×10^3

Table 2B

<i>Composition</i>	1	2	3	4	5	6	7
Polypropylene (MFI 25)	100	100	100	100	100	100	100
Polyamide 6	4	5.3	6.6	8	8	8	12
Glass fiber (Vetrotex)	20	20	20	20	20	30	30
Carbon black (EC 600)	0.67	0.88	1.1	1.5	2	1.3	2
<i>Property</i>							
Specific Gravity, Kg/dm ³	1.02	1.01	1.02	1.02	1.02	1.06	1.06
Water Absorption, %	0.04	0.06	0.06	0.04	0.05	0.08	0.08
Flexural Modulus, MPa	3984	3958	3954	3941	3936	4866	5039
Tensile Strength, MPa	54	58	52	52	58	63	63
Elongation at Break, %	2.8	3.1	2.7	2.8	2.8	2.5	2.6
Izod Impact, notched, J/m	68	85	66	63	71	85	76
Melt Flow Rate, 230 °C, 2.16Kg	5.2	4	6	2.8	3	3.3	3.2
Heat Distortion Temp, °C	161	163	161	162	163	164	163
Volume Resistivity, ohm-cm	3.24x10 ⁵	2.5x10 ³	3.2x10 ⁴	1.3x10 ³	7.9x10 ³	3.4x10 ³	1.2x10 ³

Tables 3A and 3B illustrate the dependence of resistivity and physical properties on glass fiber concentration in compositions 10 for different polypropylene/polyamide mixtures. The increase of tensile strength, modulus and flexural modulus with increasing glass fiber content is clearly appreciated.

Table 3A

<i>Composition</i>	1	2	3	4	5
Polypropylene (MFI 12)	100	100	100	100	100
Polyamide 66	5	8	12	16	16.5
Glass fiber (Vetrotex)	12	20	30	40	50
Carbon black (EC600)	1	1.5	2	2.8	2.8
<i>Property</i>					
Tensile Strength, MPa	39.4	44	56.2	58	47.4
Elongation at break, %	3.2	2.6	2.3	2.1	2
Tensile Modulus, MPa	1771	2030	2634	3133	2406
Flexural Modulus, MPa	3054	3801	4684	5394	5576
Izod Impact, notched, J/m	64	69	77	71	57
Water Absorption, %	0.02	0.03	0.04	0.06	0.07
Specific Gravity, kg/dm ³	0.981	1.025	1.082	1.122	1.145
Volume Resistivity, ohm-cm	>10 ⁸	9.4x10 ⁴	850	440	2.3x10 ⁴

Table 3B

<i>Composition</i>	1	2	3	4	5	6	7	8	9
Polypropylene (MFI 25)	100	100	100	100	100	100	100	100	100
Polyamide 66	4	5.3	6.6	8	8	6	8	10	12
Glass fiber (Vetrotex)	20	20	20	20	20	30	30	30	30
Carbon black (EC 600)	0.67	0.88	1.1	1.5	2	1	1.3	1.6	2
<i>Property</i>									
Specific Gravity, Kg/dm ³	1.02	1.00	1.01	1.04	1.02	1.05	1.06	1.0	1.06
Water Absorption, %	0.04	0.04	0.07	0.04	0.05	0.05	0.07	0.1	0.05
Flexural Modulus, MPa	391	3804	3858	373	3936	4815	4640	4732	4856
Tensile Strength, MPa	7	53	53	53	56	57	59	57	61
Elongation at Break, %	2.7	3.1	3.0	3.0	3.0	2.6	2.4	2.9	2.0
Izod Impact, notched, J/m	64	71	76	66	67	75	75	77	62
Melt Flow Rate, 275°C, 2.16Kg	18	12	11	8.6	11	8	8.8	8	6
Heat Distortion Temp, °C	161	163	163	162	162	164	165	165	163
Volume Resistivity, ohm-cm	2x1 04	9.9x10 ³	4x10 ³	490	7.9x10 ³	650	814	241	175

Table 4 illustrates the dependency of electrical resistivity of PP/PA/GF/CB systems (100/12/30/4 phr ratio respectively) on the type of second thermoplastic component (polyamide) used. It is clearly seen that any type of polyamide can be used for composition 10 and that their electrical conductivity can be determined by selecting the degree of crystallinity of the polyamide. Lower values of resistivity were

obtained for compositions 10 based on PA 66 and PA 6, PA11, PA 12 (semicrystalline polyamide) than for those based on PA 6/6-9 and PA 6-12 (amorphous polyamide). Given the same concentration of conductive additive, a higher level of conductivity was achieved in PA 66 (the most crystalline polyamide studied) based compound.

5

Table 4

<i>Property</i>	PA 66	PA 6	PA12	PA11	PA 6-6/9	PA 6-12
Tensile Strength, MPa	58.4	54.2	51.9	49.6	58.5	56.6
Elongation at break, %	2.1	1.9	2	3	2.3	1.9
Tensile Modulus, MPa	3256	3030	2541	1868	3074	3160
Flexural Modulus, MPa	4850	4699	4592	3899	4650	4890
Izod Impact, notched, J/m	72	70	68.8	58.9	61	62
Specific gravity, kg/dm ³	1.086	1.092	1.081	1.079	1.076	1.069
Volume Resistivity, ohm-cm	700	3.3x10 ³	2.3x10 ³	5.4x10 ³	3.3x10 ⁵	1.3x10 ⁵

It will also be appreciated that any type of carbon black can be used with compositions 10. Resistivity and mechanical properties of composites with five CB grades, at two loading levels, for composites based on Polypropylene (100 parts), PA 66 (12 parts) and glass fibers (30 parts) are presented in Table 5. Inspection of this table reveals that Ketjenblacks EC 300 and EC 600, the most conductive carbon blacks used provide the highest electrical conductivity.

10

Table 5

<i>Property</i>	EC600	EC 300		XC 72		CORAX L6		CONDU CTEX	
	2 phr	2 phr	4 phr	2 phr	4 phr	2 phr	4 phr	2 phr	4 phr
Tensile Strength, MPa	56.2	52.1	57.7	45.9	54	44.2	45.1	43.9	58.4
Elongation at break, %	2.1	2.5	2.3	2.6	2.3	2.6	2.2	3.1	2.1
Tensile Modulus, MPa	3133	2776	2911	2087	2933	2291	2147	2193	3194
Flexural Modulus, MPa	4684	4898	4803	4968	4747	5108	4335	4948	4638
Izod Impact, notched, J/m	77	-	72	70	68	74	66	79	72
Specific gravity, kg/dm ³	1.082	1.072	1.079	1.079	1.079	1.074	1.076	1.069	1.074
Volume Resistivity, ohm-cm	850	1560	789	>10 ⁸	4110	>10 ⁸	852	>10 ⁸	4x10 ⁴

15

Yet another factor which determines the resistivity and mechanical properties of compositions 10 is the flowability (MFI) of the polymer matrix used. As clearly seen from Table 6 below, significant lower resistivities are obtained using for example polypropylene with higher MFI. Table 6 is provided below.

Table 6

<i>Composition</i>	1	2	3	4	5	6	7	8	9
Polypropylene (MFI 3)			100						
Polypropylene (MFI 12)	100			100		100		100	
Polypropylene (MFI 25)		100			100		100		100
Polyamide 66	5	5	12	12	12	16	16	16.5	15
Glass fiber (Vetrotex)	12	12	30	30	30	40	40	50	50
Carbon black (EC 600)	1	1	2	2	2	2.8	2.8	2.8	2.5
<i>Property</i>									
Flexural Modulus, MPa	3054	3037	4168	4684	4450	5812	5515	5576	6249
Volume Resistivity, ohm-cm	10 ⁷	2863	1100	850	290	565	405	2.3x10 ⁴	543

Table 7 hereinbelow provides examples of compositions 10 including carbon fibers as also illustrated with reference to Figs. 5A - 5C hereinabove. Volume resistivity of less than 1 ohm-cm were achieved in carbon fibers/carbon black/glass fiber/second thermoplastic component (polyamide) /polypropylene compounds. Table 7 below illustrates non limiting carbon fibers containing compositions and their properties.

Table 7

<i>Composition</i>	1	2	3	4	5	6	7	8	9	10
Polypropylene (MFI 25)	100	100	100	100	100	100	100	100	100	100
Polyamide 66	12	12	12	12	12	14	14	14	14	14
Glass Fiber (Vetrotex)	30	30	30	30	30	40	40	40	40	40
Carbon Black (EC 600)	2	2	2	2	2	2.8	2.8	2.8	2.8	2.8
Carbon Fiber	0	6	10	20	30	0	6	10	14	20
<i>Property</i>										
Flexural Modulus, MPa	4850	6264	7910	9770	10514	5964	6675	8129	9641	10495
Volume Resistivity, ohm-cm	344	7.2	2	0.465	0.168	425	12.2	1.2	0.96	0.32

10

It will be appreciated that the compositions of the present invention, in particular the ones including carbon fibers and having a resistivity of less than 1 Ohm-cm provide improved Electro Magnetic Interference (EMI) shielding with a lower content of

carbon black and carbon fibers. Therefore, they are superior to prior art electrically conductive plastics in a wide range of applications, such as clean room applications where the amount of carbon is important for the cleanliness of the process.

It will be appreciated that the present invention is not limited by what has
5 been described hereinabove and that numerous modifications, all of which fall within the scope of the present invention, exist. For example, while the present invention has been described with reference to polypropylene, the present invention is equally applicable to other polyolefins such as polyethylene and to polyethylene-polypropylene mixtures. Polyethylene based compositions were prepared using LDPE and HDPE grades in a
10 generally similar manner to that of polypropylene. As an example, a polyethylene based composition (100 parts on a similar weight basis) blended with 11 parts of polyamide (PA6), 20 parts of glass fibers and 4.4 parts of carbon black (EC-300) exhibit volume resistivity of $10^5 - 10^6$ ohm-cm.

Table 8 illustrates two further examples of polyethylene based
15 compositions.

Table 8

Composition	1	2
PE 800 (MFI 20)	100	
PE 600 (MFI 7)		100
Polyamide 66	12	12
Glass fiber (Vetrotex)	30	30
Carbon black (EC 600)	2	2
Property		
Specific Gravity, Kg/dm ³	1.07	1.07
Water Absorption, %	0.06	0.06
Flexural Modulus, MPa	1663	1622
Tensile Modulus, MPa	746	678
Tensile Strength, MPa	19.3	17.1
Elongation at Break, %	3.0	3.3
Izod Impact, notched, J/m	80	81
Melt Flow Rate, 275°C, 2.16Kg	33.2	18.8
Heat Distortion Temp, °C	96	96
Volume Resistivity, ohm-cm	1x10 ⁶	2x10 ⁶

In other alternative embodiments, the polyolefin component is replaced by another thermoplastic compound as the first component forming matrix 12. In four preferred embodiments, the first component forming matrix 12 was acrylonitrile/butadiene/styrene (ABS), polystyrene (PS), high impact polystyrene (HIPS) and polyphenyleneoxide/polystyrene (NORYL).

Table 9 illustrates two examples of polyethylene-polypropylene based compositions.

Table 9

<i>Composition</i>	1	2
PE 800 (MFI 20)	100	
PE 600 (MFI 7)		100
Polypropylene (MFI 25)	24	24
Polyamide 66	8	8
Glass fiber (Vetrotex)	20	20
Carbon black (EC 600)	1.5	1.5
<i>Property</i>		
Specific Gravity, Kg/dm ³	1.03	1.02
Water Absorption, %	0.05	0.05
Flexural Modulus, MPa	1975	2117
Tensile Modulus, MPa	1246	1176
Tensile Strength, MPa	27	27.4
Elongation at Break, %	2.3	2.5
Izod Impact, notched, J/m	68	70
Melt Flow Rate, 275°C, 2.16Kg	24.7	14.2
Heat Distortion Temp, °C	101	102
Volume Resistivity, ohm-cm	3x10 ⁵	3x10 ⁵

Table 10 illustrates a nonlimiting example of compositions 10 formed with ABS, PS, HIPS and NORYL with different second thermoplastic component (different types of polyamide compositions, different glass fiber content and different low amounts (less than or equal to 3 phr) of carbon black..

Table 10

Composition	1	2	3	4	5	6
ABS	100	100	100			
PS				100		
HIPS					100	
NORYL						100
Polyamide 6		12			12	
Polyamide 12	8		12	12		
Polyamide 66						12
Glass fiber (Vetrotex)	20	30	30	30	30	30
Carbon black (EC 600)	1.2	3	3	2	3	3
Property						
Volume Resistivity,ohm-cm	10^8	10^4	10^3	10^5	10^4	10^3

5 Tables 11, 12 and 13 provide further examples of PS, HIPS and Noryl based compositions, respectively, and their mechanical properties.

Table 11 illustrates the dependence of resistivity and physical properties on glass fiber concentration in a PS/PA/GF/CB compound.

Table 11

Composition	1	2	3	4
PS (GP)	100	100	100	100
Polyamide 6	5	8	12	
Polyamide 12				12
Glass fiber (Vetrotex)	12	20	30	30
Carbon black (EC 600)	1.5	2	3	3
Property				
Specific Gravity, Kg/dm ³	1.09	1.17	1.22	1.2
Water Absorption, %	0.12	0.12	0.13	0.07
Flexural Modulus, MPa	4850	5830	7100	7000
Tensile Modulus, MPa	2740	3130	3650	3290
Tensile Strength, MPa	56	70	66	59
Elongation at Break, %	2	2	2	2
Izod Impact, notched, J/m	43	52	51	38
Melt Flow Rate, 230 °C, 2.16Kg	8.2	5.7	3.7	3.0
Heat Distortion Temp, °C	82	84	-	86
Volume Resistivity, ohm-cm	4.5x10 ⁵	7.5x10 ⁴	3.8x10 ⁴	2.2x10 ⁴

Table 12 illustrates the dependence of resistivity and physical properties on glass fiber concentration in HIPS/PA/GF/CB compound.

Table 12

Composition	1	2	3	4
HIPS	100	100	100	100
Polyamide 6	5	8	12	
Polyamide 12				12
Glass fiber (Vetrotex)	12	20	30	30
Carbon black (EC 600)	1.5	2	3	3
Property				
Specific Gravity, Kg/dm ³	1.12	1.16	1.21	1.19
Water Absorption, %	0.13	0.14	0.14	0.07
Flexural Modulus, MPa	3600	4560	6410	6050
Tensile Modulus, MPa	1800	2050	2630	2050
Tensile Strength, MPa	43	51	61	46
Elongation at Break, %	2	2	2	2
Izod Impact, notched, J/m	46	46	47	34
Melt Flow Rate, 230 °C, 2.16Kg	2.3	1.7	1.9	1.7
Heat Distortion Temp, °C	-	97	92	93
Volume Resistivity, ohm-cm	9x10 ⁶	7x10 ⁴	7x10 ³	1.5x10 ⁴

Table 13 illustrates the dependence of resistivity and physical properties on glass fiber concentration in Noryl/PA66/GF/CB compound.

Table 13

Composition	1	2
Noryl	100	100
Polyamide 66	12	16
Glass fiber (Vetrotex)	30	40
Carbon black (EC 600)	3	4
Property		
Specific Gravity, Kg/dm ³	1.24	1.28
Water Absorption, %	0.17	0.20
Flexural Modulus, MPa	6501	7193
Tensile Modulus, MPa	3382	4361
Tensile Strength, MPa	64.1	79.2
Elongation at Break, %	2.0	1.8
Izod Impact, notched, J/m	38	42
Melt Flow Rate, 275°C, 2.16Kg	1.0	0.5
Heat Distortion Temp, °C	122	124
Volume Resistivity, ohm-cm	5x10 ⁵	1.8x10 ⁴

Table 14 illustrates compositions 10 wherein the second thermoplastic component is EVOH and notpolyamide. The table illustrates the dependence of resistivity on glass fiber concentration in PP/EVOH/GF/CB compound.

Table 14

Composition	1	2	3
Polypropylene (MFI 25)	100	100	100
EVOH	8	10	12
Glass fiber (Vetrotex)	20	30	30
Carbon black (EC 600)	2	2.5	3
Property			
Specific Gravity, Kg/dm ³	1.03	1.07	1.07
Water Absorption, %	0.03	0.03	0.05
Flexural Modulus, MPa	4530	5697	5529
Tensile Modulus, MPa	2475	2572	2670
Tensile Strength, MPa	59.7	62.1	61.8
Elongation at Break, %	2.7	2.5	2.4
Izod Impact, notched, J/m	69	66	58
Melt Flow Rate, 230°C, 2.16Kg	5.0	4.5	3.2
Heat Distortion Temp, °C	160	160	160
Volume Resistivity, ohm-cm	1.7x10 ⁵	1.6x10 ⁵	1.2x10 ³

Table 15 illustrates the dependence and resistivity and physical properties on glass fiber concentration in PP/PA/GF/CB (PP: Elastomer 60:40) compound containing elastomer. It is clearly shown that the compounds containing elastomer offer higher impact than the compounds summarized in Table 3B.

Table 15

Composition	1	2	3	4
Polypropylene	100	100	100	100
Polyamide 66	5	8	8	10
Glass fiber (Vetrotex)	12	20	25	30
Carbon black (EC 600)	1	1.5	1.5	2
Property				
Flexural Modulus, MPa	1500	1900	2000	2300
Izod Impact, notched, J/m	134	120	107	100
Surface Resistivity, ohm/sq.	10^7	10^6	10^5	10^5

It will be appreciated by persons skilled in the art that the present invention is not limited to what has been particularly shown and described hereinabove.

- 5 Rather, the scope of the present invention is defined only by the claims that follow:

CLAIMS

1. An electrically conductive composition comprising:
a matrix comprising substantially a first thermoplastic component;
5 a second thermoplastic component having a higher polarity than that of said first thermoplastic component, said second component encapsulating a plurality of fibers forming a network of encapsulated fibers within said matrix; and
a carbon component preferentially attracted to said second component so as to make said network an electrically conductive network within said matrix.
- 10 2. A composition according to claim 1 wherein said first thermoplastic component is a polyolefin compound with or without an added elastomer component.
3. A composition according to claim 2 wherein said polyolefin is selected from the group consisting of polypropylene and polyethylene
4. A composition according to claim 3 wherein said polypropylene is a
15 homopolymer or a copolymer.
5. A composition according to claim 1 wherein said second component is polyamide or EVOH.
6. A composition according to claim 5 wherein said composition comprises less than 20 parts per hundred polyamide or EVOH.
- 20 7. A composition according to claim 1 wherein said fibers are glass fibers.
8. A composition according to claim 7 wherein said composition comprises less than 55 parts per hundred glass fibers.
9. A composition according to claim 1 wherein said carbon component is carbon black .
- 25 10. A composition according to claim 1 wherein said carbon component is carbon fibers.

11. A composition according to claim 1 wherein said carbon component is a mixture of carbon black and carbon fibers.
12. A composition according to claim 9 comprising less than 10 parts per hundred carbon black.
- 5 13. A composition according to claim 10 comprising less than 30 parts per hundred carbon fibers.
14. A composition according to claim 1 having a volume resistivity from about 0.1 to about 10^9 ohm-cm.
15. A composition according to claim 1 having a flexural modulus of up to
10 about 11,000 MPa.
16. A composition according to claim 9 having a tensile strength of up to 60 MPa.
17. A composition according to claim 1 wherein said first component is selected from acrylonitrile/butadiene/styrene, polystyrene, high impact polystyrene and
15 polyphethyleneoxide/polystyrene.
18. A composition according to claim 17 wherein said second component is polyamide or EVOH.
19. A composition according to claim 2 wherein said elastomer component comprises a combination of elastomers.
- 20 20. A composition according to claim 19 wherein said combination of elastomers affect the mechanical properties of said composition without significantly affecting its electrical conductivity.
21. A method for producing an electrically conductive composition comprising the step of compounding a matrix comprising substantially a first
25 thermoplastic component with a second thermoplastic component having a higher polarity than that of said first thermoplastic component, said second component encapsulating a plurality of fibers forming a network of encapsulated fibers within said matrix; and

a carbon component preferably attracted to said second component so as to make said network an electrically conductive network within said matrix.

22. A method according to claim 21 further comprising the step of forming said first thermoplastic component from a polyolefin compound with or without an added elastomer component.
23. A method according to claim 22 wherein said polyolefin is selected from the group consisting of polypropylene and polyethylene.
24. A composition according to claim 23 wherein said polypropylene is a homopolymer or a copolymer.
- 10 25. A composition according to claim 21 further comprising the step of forming said second thermoplastic component from polyamide or EVOH.
26. A method according to claim 25 wherein said composition comprises less than 20 parts per hundred polyamide.
27. A method according to claim 21 wherein said fibers are glass fibers.
- 15 28. A method according to claim 27 wherein said composition comprises less than 55 parts per hundred glass fibers.
29. A method according to claim 21 wherein said carbon component is carbon black .
30. A method according to claim 21 wherein said carbon component is carbon fibers.
- 20 31. A method according to claim 21 wherein said carbon component is a mixture of carbon black and carbon fibers.
32. A method according to claim 29 comprising less than 10 parts per hundred carbon black.
- 25 33. A method according to claim 30 wherein said composition comprising less than 30 parts per hundred carbon fibers.

34. A method according to claim 21 wherein said composition has a volume resistivity from about 0.1 to about 10^9 ohm-cm.
35. A method according to claim 21 wherein said composition has a flexural modulus of up to about 11,000 MPa.
- 5 36. A method according to claim 29 wherein said composition has a tensile strength of up to 60 MPa.
37. A method according to claim 21 comprising the step of forming said first component from acrylonitrile/butadiene/styrene, polystyrene, high impact polystyrene and polyphenyleneoxide/polystyrene.
- 10 38. A method according to claim 37 wherein said second component is polyamide or EVOH.
39. A method according to claim 21 wherein said elastomer component comprises a combination of elastomers.
40. A method according to claim 39 wherein said combination of elastomers
15 affect the mechanical properties of said composition without significantly affecting its electrical conductivity.

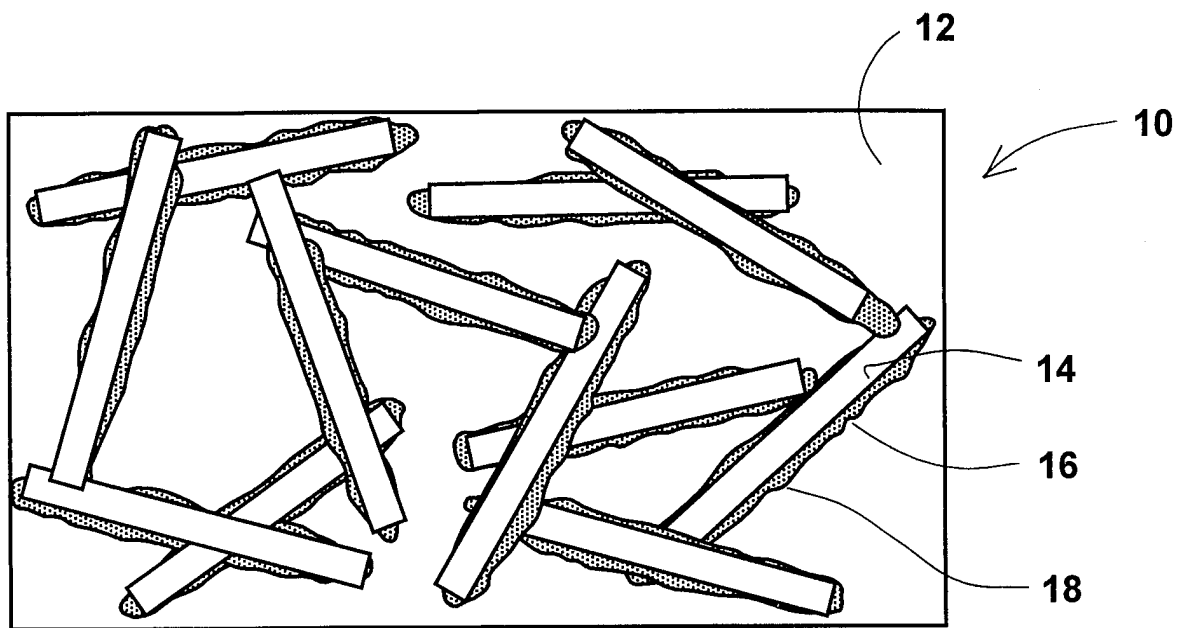


FIG. 1

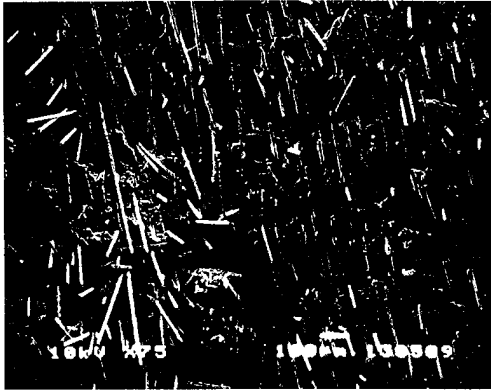


FIG. 2a

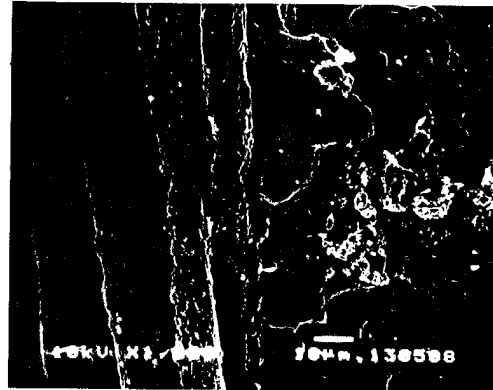


FIG. 2b

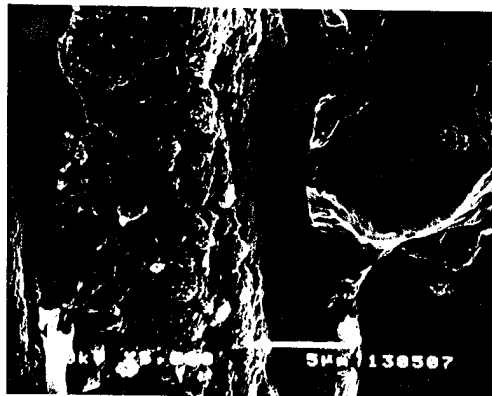


FIG. 2c

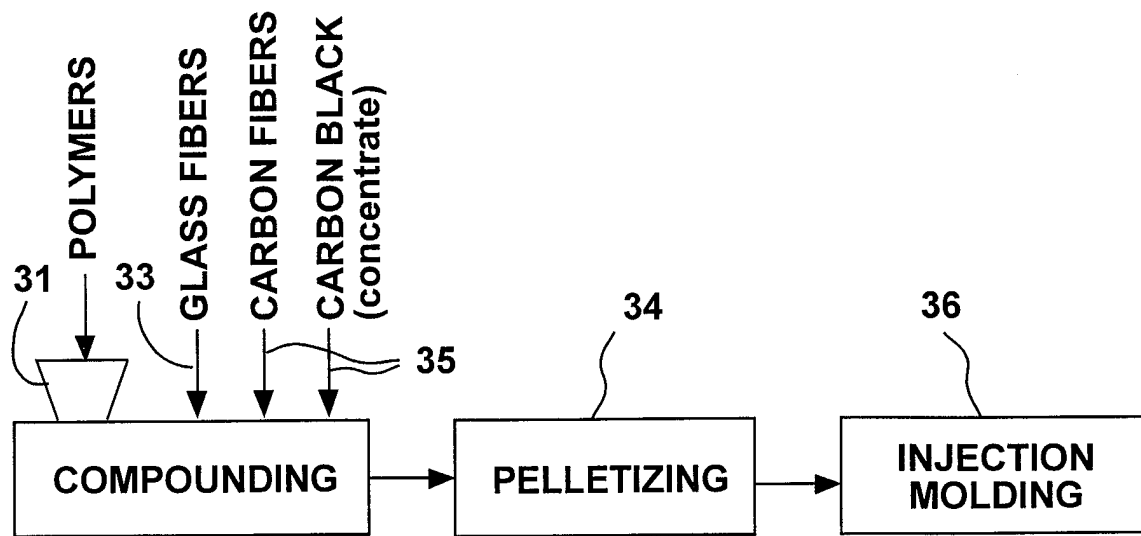
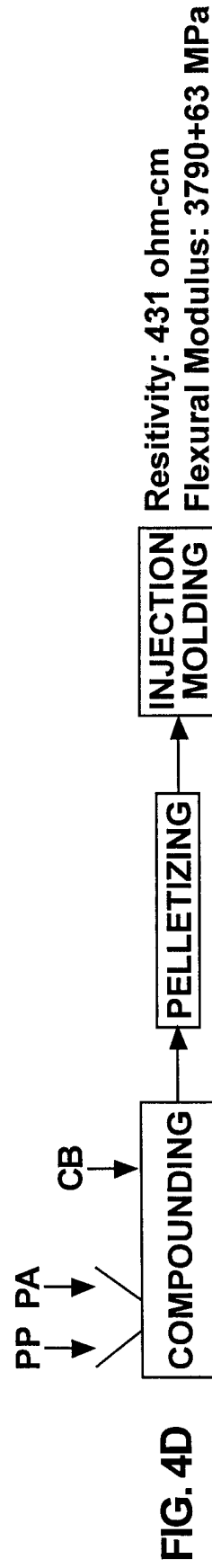
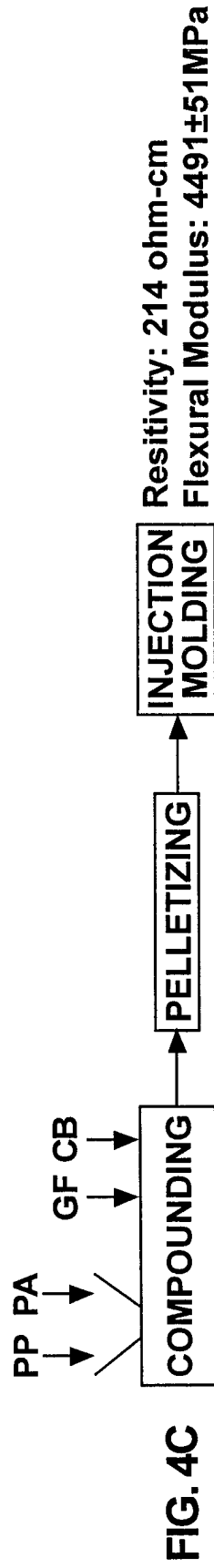
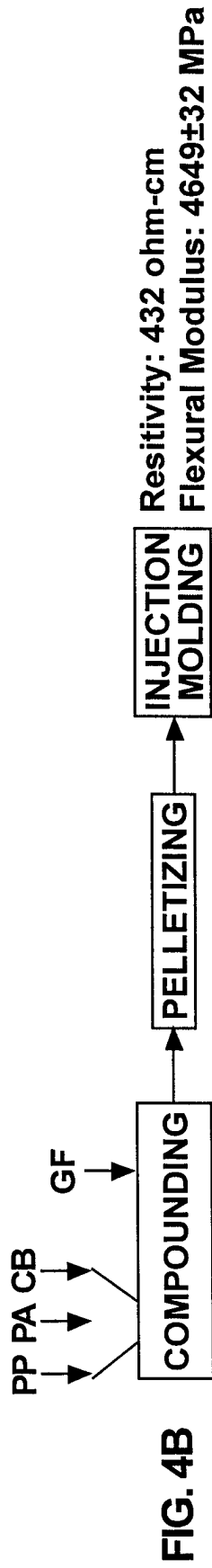
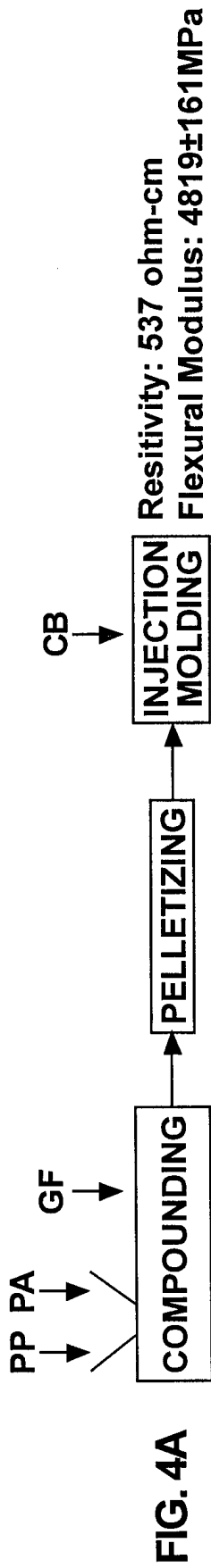
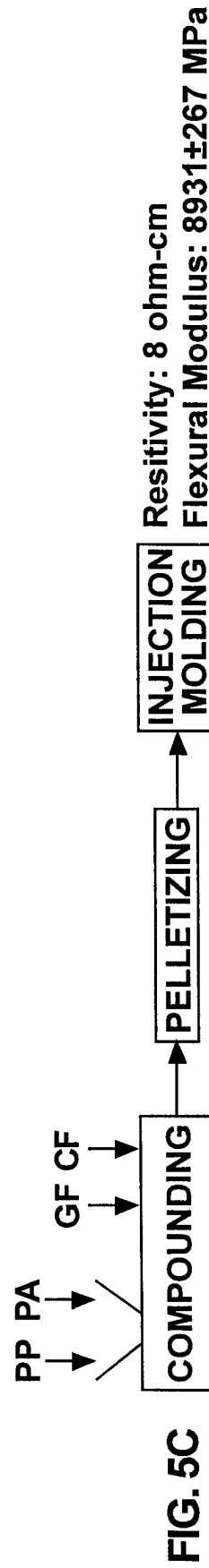
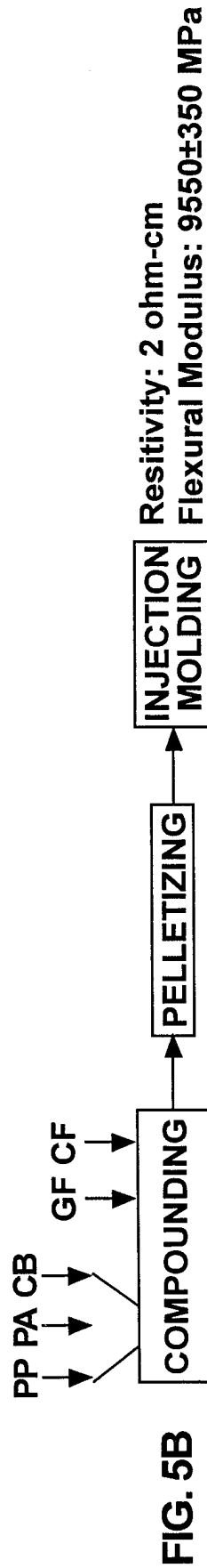
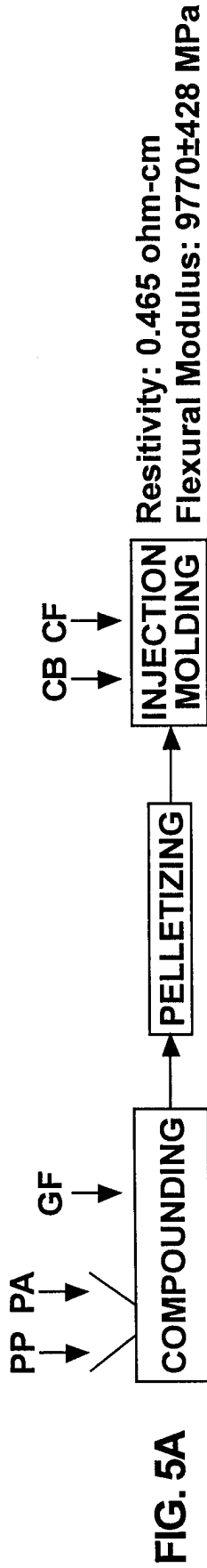


FIG. 3





time →

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL97/00342

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) :H01B 1/24; C04B 35/52. US CL : 252/511; 264/105. 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) U.S. : 252/511; 264/105. 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) APS (terms include: glass fiber#, polyamide#, carbon fiber#, carbon black, thermoplastic#)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,248,553 A (MIYASHITA ET AL) 28 September 1993 (28-09-93), abstract; column 3, lines 22-65; claims.	1, 9-17, 21, 27-40
X	US 5,004,561 A (NOMURA ET AL) 02 April 1991 (02-04-91), abstract; column 2, lines 24-40; Col 4, lines 55-60.	1-40
X	US 5,098,610 A (OKAMURA ET AL) 24 March 1992 (24-03-92), abstract; column 2, lines 1-22; examples.	1-4, 7-17, 19-24, 27-37, 39-40
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*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	
*A document defining the general state of the art which is not considered to be of particular relevance	*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	
*E earlier document published on or after the international filing date	*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	
*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)	*A document member of the same patent family	
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Date of the actual completion of the international search 05 FEBRUARY 1998	Date of mailing of the international search report 04 MAR 1998	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Mark Kopec</i> MARK KOPEC Telephone No. (703) 308-0661	