

Description**Field of the Invention**

5 This invention relates to metal/polymer composites, and particularly to such composites which have a layer comprising a plurality of fine metal strands. The invention also relates to a method of squirting fine metal strands onto a substrate.

Background of the Invention

10 A variety of different metal and polymeric composites are known and are used in many, varied applications. One important use for a metal/polymer composite is as a shield for a variety of electromagnetic and radio frequency waves. Such waves, which cause interference in a variety of devices, are commonly referred to as electromagnetic interference (EMI) and radio frequency interference (RFI) (hereinafter jointly referred to as EMI). Shielding from EMI is often placed around an EMI source to prevent it from radiating EMI and interfering with surrounding devices. Also, the devices themselves may be provided with EMI shielding in an effort to shield the device from incoming EMI.

Another important use for a metal/polymer composite is for the protection of sensitive electronic parts from static charges. Static charge build-up can result from, for example, friction between surfaces, and can lead to a build-up of a high electrical potential. A sensitive electronic part that may come into proximity or contact with a statically charged surface can be destroyed or damaged. During shipping or handling, shielding of an electronic part from static electricity can be accomplished by placing the part in an electrically conductive metal or metal/polymer container, with the metal providing a preemptive surface to drain away any static charge.

25 Metal is a well-known, effective shield against EMI. However, many applications require that the shielding be transparent, while also being electrically conductive to aid in the dissipation of EMI. In addition, many applications require that the EMI shielding be thermoformed into a required shape or structure. A thermoforming process comprises heating the material and forming the material into the desired shape. As used herein, thermoforming refers to both stretching a material while heated and also heat-shrinking a material. Metal is also relatively heavy compared to polymeric materials, and therefore, where weight is a factor the amount of metal is desirably reduced.

Another desirable characteristic of an EMI or static shielding is of course cost. Since many metals are relatively expensive, it is desirable to be able to utilize sufficient metal to accomplish the objective, while closely tailoring the amount of metal to that desired amount. This also allows the weight of the composite to be kept to a minimum.

In addition to the cost of the metal itself, metal fabrication is generally a costly procedure. Separately fabricating a wire mesh or screen for lamination to a polymer is relatively costly. Further, handling of wire meshes can present difficulties, especially for fine meshes or screens of soft metals.

40 Metal-polymer blends have been described for use in EMI shielding, as for example in EP-A-0132739. Such metallized polymer blends require the processing step of blending together a polymer and metal at molten temperatures. Further, the polymer must be processed with a high amount of metal to provide a metal component that is continuously touching for effective electrical conductivity throughout the composite. Also, the metal-polymer blends would not be expected to be transparent.

45 Metal/polymer composites having continuous coatings of metal are known. Continuous metal coatings are typically deposited by vapor deposition, sputtering or the like. To obtain coatings thick enough for good electrical conductivity, such processes are typically time consuming and relatively expensive. Also, such coatings are not transparent, and are therefore undesirable for certain uses.

Therefore, a need exists for an economical metal/polymer composite which may be used, for example, in EMI or static shielding. There is also a need for a metal/polymer composite which is electrically conductive, transparent, and which, if desired, is able to be thermoformed, without loss of either electrical conductivity or transparency. There is also a need for such a metal/polymer composite which includes precisely arranged fine metal strands, the amount of metal closely tailored to that amount necessary to accomplish the desired task. There is a further need for a metal/polymer composite with a metal layer comprising a plurality of fine metal strands in a random configuration. Further, there is a need for a method of making a suitable metal/polymer composite without the need for separate fabrication of a metal structure, such as a wire mesh or screen.

Summary of the Invention

The present invention provides a metal/polymer composite, with a discontinuous metal layer, formed from a plurality of fine metal strands, which may be used, for example, in static or EMI shielding. The metal/polymer composite may be electrically conductive in one or more directions or locally conductive as desired. The discontinuous metal layer may also be transparent. The metal may be selected so that the composite is capable of being thermoformed without loss of electrical conductivity or transparency.

The metal/polymer composite comprises a polymeric substrate including a discontinuous metal layer. The metal layer comprising a plurality of fine metal strands provided on the substrate, the metal strands individually having a cross section with an area of about 100 to 100,000 μm^2 and the cross section having a flat portion and an arcuate portion. Where thermoformability is desired, the metal has a melting point of less than the softening or melting temperature of the polymeric substrate.

The metal may be arranged in a number of configurations. One preferred embodiment is a mesh configuration comprising a plurality of regularly spaced, horizontal and vertical strands substantially perpendicular to each other. The strands of metal may be spaced precisely at extremely close spacings, for example, spaced at an average spacing of between 2 and about 200 strands per cm. The metal layer may also be a random wandering pattern of a plurality of fine strands of metal.

The present invention also includes a method of forming a metal/polymer composite comprising the steps of: (a) providing a polymeric substrate having a conductor support surface; and (b) squirting a plurality of molten metal strands onto said conductor support surface in a desired pattern.

As used herein, "transparent" means allowing at least portions of visible light to pass therethrough. The amount of optical clarity which is required will vary with the desired end use of the composite. "Electrically conductive" means at least locally electrically conductive in at least one direction. "Discontinuous" means that a metal film or foil is not used, but rather continuous or substantially continuous metal strands are arranged on a surface. "Fine" means a strand having a cross sectional area which is less than 100,000 μm^2 .

Brief Description of the Drawings

Figure 1 is a schematic plan view of a uniform mesh configuration of the present invention.

Figure 2 is a schematic plan view of a regular sine wave configuration of the present invention.

Figure 3 is a schematic plan view of an opposed sign wave configuration of the present invention.

Figure 4 is a schematic plan view of a cross-hatched configuration of the present invention.

Figure 5 is a schematic side view of one step in the method of the invention depicting the metal strand being deposited onto a moving substrate.

Figure 6 is a cross-section of a single metal strand along 6-6 of Figure 4.

Figure 7 is a photograph depicting a random configuration of the present invention.

Detailed Description of the Invention

The present invention provides a metal/polymer composite which comprises a plurality of fine metal strands provided on a polymeric substrate. The composite is electrically conductive, and can be transparent and thermoformable. The invention also provides a method of squirting fine metal strands onto a substrate in a desired configuration, ranging from precise evenly spaced lines to a random, wandering configuration.

The metal/polymer composite comprises a polymeric substrate with strands of metal and squirted thereon in the desired configuration. The metal layer is a discontinuous layer comprised of a plurality of metal strands. To allow thermoforming of the metal/polymer composite without loss of electrical conductivity or transparency, the melting point of the metal is less than the softening or melting temperature of the polymeric substrate.

Substrates

A wide range of polymers are suitable for use as substrates in the present invention. Where it is advantageous for the composite of the present invention to allow substantial portions of visible light to pass therethrough, it is desirable that the material selected as the polymeric substrate be at least partially transparent to the visible region of light. In many applications, it may not be necessary that the polymer have a glass-like transparency, and in many cases this may be undesirable. The polymer may be cloudy, colored, partially opaque or the like, as required by the particular end use.

Where it is desired that the metal/polymer composite be thermoformable, the polymeric material selected as the substrate should be able to be formed under heat and pressure into the desired configuration (thermoformed). The thermoforming process may stretch the heated polymer, for example, to preferably at least 50 percent and more preferably, at least 200 percent, or it may shrink when heated to, for example, at least 25 percent less than its original dimensions. In addition, in some applications only certain regions of the composite are stretched, for example, to greater than 200 percent of the local or regional dimension.

Suitable polymers for use in the composite of the present invention include polyamides; polyolefins, including ethylene, propylene, methylpentene and blends thereof; polyurethanes; polysulfones; polycarbonates; linear polyesters, such as polyethyleneterephthalate and polybutylene terephthalate; cellulose esters, such as cellulose acetate, and cellulose propionate; halogenated polyolefins; polyacetals; ABS (acrylonitrile butadiene styrene) resins; polyphenylene oxide plus styrene resin (Noryl®); the alkenyl aromatic resins typified by polystyrene, styrene copolymers, blends and graft copolymers; and the alkenyl aromatic resins typified by polystyrene copolymers. Included in the term polymer are homopolymers, oligopolymers and blends of two or more polymeric materials.

Preferred polymers include a polyester formed from terephthalic acid and one or more diols selected from the group consisting of ethylene glycol, propylene glycol, 1,4 butane diol, 1,6 hexane diol, and 1,4 cyclohexane dimethanol.

In addition to polymers, the method of the present invention may be used to provide a plurality of fine metal strands onto the surface of a non-polymeric substrate such as ceramic, glass, metal and the like. The use of certain substrates may require a primer layer or coating to enable the metal strands to adhere to the substrate. In certain applications, it may be desirable that the metal strands do not adhere well to the substrate, for example, when transferability of the metal strands is desired. In such cases, a non-adhering substrate such as a polyimide may be utilized.

Metals

A wide variety of metals may be used. Where thermoformability is desired, a metal having a melting point of less than the softening point or melting temperature of the polymer, is utilized. Examples of preferred metals for use in the composite of the present invention include tin, lead, bismuth, zinc, indium, aluminum, and their alloys (including alloys of these metals with higher melting point metals), and mixtures thereof. Higher melting point metals are also suitable where thermoformability is not desired.

The metals, metal alloys or mixtures of metals and metal alloys are preferably utilized in a substantially pure form. It is unnecessary, and often undesirable, to include polymeric binders which are found, for example, in metal inks, or other fillers or additives. The metal is applied in a molten state through a fine orifice, such as a capillary or needle. Therefore, it is preferable that the metal not include substances which could clog or otherwise hamper the application of the typically fine strand of metal, which is applied to the conductor support surface of the polymer.

The metal is substantially undrawn when it solidifies from the molten state in which it is applied to the substrate. Many screens and other mesh configurations which are woven from fine strands of metal are drawn or stressed during processing.

The metal layer of the present invention comprises a plurality of fine metal strands individually having a cross section with an area of about 100 to 100,000 μm^2 . The cross section of the individual strands is preferably 100 to 10,000 μm^2 , and where very fine strands are desired, such as in use in static control shielding, the cross sectional area is about 100 to 7500 μm^2 . Because the method of the present invention applies the metal strand onto the substrate in the form of a molten metal, the cross section of the individual strands will include a flat portion and an arcuate portion. The flat portion of the individual strands being that portion of the metal strand in contact with the substrate. As is discussed in more detail hereinbelow, the cross section of the individual strands is varied depending upon the angle at which it is deposited onto the substrate. The cross section of the individual strands may vary from almost a complete circular cross section, with a small flat portion, to a larger flat portion and an arcuate portion representing a small segment of a circle. In addition, where the fine metal strands are provided in an intersecting arrangement, such as a mesh or random intersecting configuration, the plurality of fine metal strands will have a plurality of fused junctions. The intersections will be fused because one or both of the strands will be in the molten form when the junction therebetween is formed.

Method of Making

The present invention also includes a method for applying molten fine metal strands to a substrate to make a metal/polymer composite. The metal layer of the composite comprises fine strands of metal arranged in a variety of configurations including precisely and regularly spaced strands and random or wandering configurations of strands. The metal layer is provided in a desired configuration on the surface of a substrate.

In general terms, the method of the invention comprises the steps of: (a) providing a polymeric substrate; and (b) squirting a plurality of molten metal strands onto a surface of the substrate. If thermoformability is desired, the metal has a melting temperature of less than the softening or melting temperature of the polymeric substrate. The metal is provided in a desired pattern which may vary from extremely precise to extremely random. If transparency is desired, the metal layer configuration should allow substantial portions of visible light to pass therethrough. The method may also be used to make a pattern which is opaque.

The metal/polymer composite may be thermoformed into a desired shape or configuration, suitable for the desired end use. In thermoforming, the composite is typically stretched at least 50 percent and often 200 percent and more. Composites of the present invention are capable of being thermoformed and stretched while retaining electrical conductivity and transparency. In addition, it may be desirable to heat-shrink the composite, again while maintaining electrical conductivity and transparency of the metal/polymer composite.

Referring to Fig. 1, a metal/polymer composite 10 is shown having a metal pattern 12 on a polymeric substrate 13. The metal pattern 12 is in a mesh configuration having horizontal strands 14 and vertical strands 16 which are substantially perpendicular to the horizontal strands 14. The horizontal and vertical strands 14 and 16 are regularly spaced apart at desired intervals. The strands 14 and 16 intersect at a plurality of fused junctions 15. The mesh pattern 12 provides electrical conductivity in both X and Y directions. A configuration like that shown in Fig. 1 with more than one set of parallel lines can be made by depositing a single direction set of lines on a substrate and laminating two or more such substrates together in the desired configuration, such as perpendicular.

Referring to Fig. 2, a second configuration of a metal/polymer composite 20 is shown having a metal pattern 22 on a polymeric substrate 23. The pattern 22 is in the shape of sine waves which are closely spaced at regular intervals. Each metal strand 24 has a sine wave configuration. Each sine wave has a similar period so that the sine waves do not cross thus providing electrical conductivity in the X direction but not in the Y direction.

Referring to Fig. 3, a metal/polymer composite 30 is shown having a metal pattern 32 on a polymeric substrate 33, which is made up of metal strands 34, each metal strand 34 having the shape of a regularly repeating sine wave. The metal strands 34 are oppositely opposed so that a plurality of fused junctions 36 are provided.

Referring to Fig. 4, an additional embodiment of the invention is shown, a metal/polymer composite 40 having a metal pattern 42 on a polymeric substrate 43. The pattern 42 which includes horizontal strands 44 and a periodic bisector 46 which has a zigzag configuration providing electrical connection between the horizontal strands 44 at a plurality of fused junctions 48.

Referring to Fig. 5, a step in the method of the present invention is shown. A metal dispenser generally designated 50 having a vessel portion 52, and a nozzle portion 54 with an orifice 56, is shown. The vessel 52 of the dispenser 50 contains a molten metal 60. The molten metal 60 is squirted through the orifice 56 in the form of a fine metal strand 62. A substrate 70, moving in the direction of the arrow, is moved past the orifice 56 to provide the thin metal strand 62 on a substrate surface 72. The angle between the nozzle 54 and the substrate surface 72 has been designated alpha.

Referring to Fig. 6 a cross-sectional view along the line 6-6 of Fig. 5 is shown. The metal strand 62 in cross-section is shown on the substrate surface 72. The semicircular cross-section of the strand 62 may be varied by varying the angle alpha shown in Fig. 5 as well as the speed of the substrate 70. The strand has an arcuate portion 74 and a flat portion 76. When the angle alpha is small the cross-section of the metal strand 62 will be almost circular having a relatively small flat portion. As the angle alpha increases the cross-section flattens and the arcuate portion becomes a smaller segment of a circle with a longer flat portion.

Referring to Fig. 7, a photograph showing a metal/polymer composite of the invention is shown. The metal layer is comprised of a plurality of randomly configured fine metal strands intersecting at various and random fused junctions. The metal layer is electrically conductive in both the X and the Y directions because of the plurality of intersections between the metal strands. The metal/polymer composite shown in

Fig. 7 is substantially transparent.

The desired pattern, such as those shown in Figures 1-4 and 7, can be produced through a number of means. A plurality of metal dispensers, such as the dispenser 50 in Fig. 5, may be positioned at the desired intervals. In addition, by means of a lathe, the dispenser can be traversed longitudinally while the substrate is rotated at a desired number of revolutions per minute to provide a fine, regular spacing between the strands of metal. The substrate may then be rotated, for example, 90 degrees, and the process repeated to provide a similar repeating configuration of strands in a perpendicular direction.

By utilizing orifices of various diameters and by varying the method of providing the metal strand to the substrate, such as by rotating a substrate on a mandrel, extremely precise and closely-spaced, regular configurations of metal strands may be produced. For example, one preferred embodiment includes strands which are regularly spaced at an average spacing of about 2 to 200 strands per cm. Such strands may be provided, for example, perpendicular to each other, to provide a regularly spaced mesh configuration, or they may be provided, for example, in three directions intersecting each other at 60-degree angles.

In addition, the fine metal strands may be configured in a random configuration such as that shown in Fig. 7. Under certain conditions when a molten metal jet is squirted into air it encounters resistance from the viscosity of the air; this resistance slows the stream and causes the jet to bunch up and become wavy or sinuous at a certain distance from the orifice. The waviness in the molten stream increases with increasing distance from the orifice. When this sinuous jet encounters a moving substrate, the resulting patterns of metal strands on the substrate are also sinuous. Both the average amplitude of the waves and their degree of randomness increases with increasing substrate to orifice distance. The randomness of the pattern is also enhanced by using slower substrate speeds relative to the jet velocity.

The composites of the present invention can be made with fine strands of metal in configurations which block less than 5 percent of the visible light transmitted through the metal configuration. Such composites may be useful where transparency of the composite is desired.

The metal/polymer composites of the present invention may be thermoformed without loss of electrical conductivity or transparency where the melting point of the metal is less than the softening point or melting temperature of the polymer. The metal/polymer composite may be thermoformed into any of a number of shapes or configurations, including a variety of relief patterns, such as a plurality of square, round, triangular, or octagonal cavities or the like.

It may be desirable to press the metal layer of the metal/polymer composite of the present invention into the conductor surface of the polymer so that the metal layer is flush with the conductor surface. This configuration can improve the scratch resistance and durability of the fine metal lines of the metal layer. Such a configuration can be made, for example, by passing the metal/polymer composite through a set of heated rollers to press the metal into the polymer.

The invention is further described in the following non-limiting examples.

Example 1

A thermoformable metal/polymer composite of the invention was made as follows: a 14 mm internal diameter (I.D.), 0.9 m long Pyrex glass tube, was heated at its midpoint using a propane torch and then gently pulled apart and pinched off to make two, 0.4 m tubes, each with one end whose inside diameter was tapered down to a capillary. The capillary end of one tube was then carefully abraded with #400 grit abrasive paper until the tube had a nozzle opening of 0.15 mm in diameter. The tube was then wrapped with 1.22 m of a 208 watt, 12.5 mm wide resistance heating tape (manufactured by Thermolyne Corp). The glass tube and resistance tape was mounted vertically in a clamping assembly which was mounted on the tool carriage of a lathe. The glass tube was positioned so that the nozzle was spaced 2 mm above a 7.7 cm diameter aluminum mandrel positioned in the chuck of the lathe. A 23 cm by 23 cm by 0.25 mm piece of cast polyethylene terephthalate (PET) sheet was taped to the curved surface of the mandrel with one edge parallel to the cylindrical axis of the mandrel. The glass tube was heated and filled to a height of 30 cm with a 34 wt% bismuth, 66 wt% indium alloy which had been previously melted and heated to 250 °C. The metal in the tube exerted a pressure of 25 kPa. A molten jet of metal formed immediately. The lathe was then operated to spin the mandrel at 250 rpm giving a mandrel surface speed of 1 m/sec. The glass tube was advanced by the carriage in a longitudinal direction at a feed rate so as to give 3.175 mm of longitudinal movement for every revolution of the mandrel. The nozzle was positioned so that the metal jet intersected the PET at roughly 90°. A line of metal was thus drawn onto the surface of the PET to create a set of parallel spaced metal lines 3.175 mm apart. The molten metal instantly solidified upon contact with the PET. After the surface of the PET was completely covered with evenly spaced metal lines, the lathe was stopped and the PET piece was rotated 90° and retaped to the mandrel. The lathe was again operated as

before to create a second set of parallel metal lines which intersected the first set at 90° making a square pattern of 3.175 mm spaced lines. The lines were 0.3 mm wide and roughly 0.1 mm thick. The resulting sample was placed into a Long® stretcher, heated to 150°C and stretched simultaneously along two perpendicular axes parallel to the square edges of the film. The film was stretched 250 % in both directions without the lines losing their electrical conductivity.

Example 2

A metal/polymer composite similar to that described in Example 1 was made, except that the 7.7 cm diameter aluminum mandrel was replaced with a 15.4 cm diameter aluminum mandrel, and the glass tube and nozzle were replaced with a 1.28 cm diameter by 0.6 m long stainless steel tube with a #27 G 1/2 Becton Dickinson Co. hypodermic needle brazed into one end. The needle was pinched off slightly, giving it an effective nozzle diameter of 200 m. The stainless steel tube was filled to a level 0.46 m above the nozzle with a 42 wt% tin, 58 wt% bismuth alloy which had been previously melted and heated to 250°C. As in Example 1, the metal lines were substrate taped to the aluminum mandrel. A 36 cm by 36 cm by 0.25 mm piece of Kodar® PETG copolyester 6763 manufactured by Eastmann Kodak was used as the substrate. The lathe was spun at 250 rpm giving a mandrel surface speed of 2 m/sec. The lathe carriage was fed at a constant rate of 3.1 mm per revolution. Two sets of parallel metal lines were drawn on the substrate. The lines in each set were 3.1 mm apart and the sets of lines intersected one another at roughly 90°. The width of the lines was 0.4 mm and the thickness was roughly 0.1 mm at the center of the line. The metal pattern was tested for thermoformability by vacuum thermoforming the sample using a die which had an array of ten 2.5 cm by 1.9 cm by 1.3 cm deep cavities. The PETG substrate was heated for 15 seconds in the thermoformer heater which was set to 316°C, and then vacuum formed with the surface of the PETG substrate having the metal lines away from the forming die. In places the lines on the resulting thermoformed sample stretched 250 % in two perpendicular directions without losing electrical conductivity.

Example 3

A metal/polymer composite was prepared as follows: a 46.15 cm long, 14 mm ID quartz glass tube was prepared in a manner similar to that used to prepare the tube in Example 1, except that an oxygen-acetylene torch was used to melt the quartz to form a nozzle. The resulting tube had a nozzle diameter of 0.13 mm. It was clamped onto the lathe carriage in a manner similar to Example 1. A 48 wt% tin, 52 wt% indium alloy was heated to 250°C and poured into the tube. The tube was then pressurized using Argon gas. The orifice of the tube was positioned 2 mm from the aluminum mandrel. A series of experiments were then carried out to study the variables of pressure, substrate speed, and nozzle angle. Cast PET substrates of 36 cm by 36 cm by 0.25 mm were used in these experiments. In the first experiment, the lathe rotational speed was set to 250 rpm (2 m/sec surface speed). The angle between the nozzle and the substrate was a constant 45° measured between the jet and the tangent to the substrate in the direction of the approaching substrate. The pressure was slowly increased as the nozzle was swept longitudinally at a constant rate of 3.1 mm per revolution. Continuous lines did not form until the pressure reached 48 kPa. Between 48 and 138 kPa the line width increased from 0.25 mm to 0.7 mm but the line thickness stayed constant at 0.08 mm.

Example 4

A composite as described in Example 3 was made except that the nozzle pressure was held constant at 90 kPa and the substrate speed was varied from 1.7 m/sec (214 rpm) to 3.97 m/sec (500 rpm). The resulting lines had a constant width of 0.5 mm but the thickness changed from 0.1 mm to 0.04 mm.

Example 5

A composite as described in Example 3 was made except that the nozzle pressure was kept constant at 90 kPa and the substrate speed was kept constant at 2 m/sec (250 rpm). The nozzle angle was changed from 150° to 20°. The main effect was a change in the shape of the lines from a flat line of 1.2 mm width and 0.03 mm thickness at 150° to a semicircular line of 0.3 mm width and 0.1 mm thickness at 20°.

Example 6

A composite was made on a 15 cm by 45 cm by 0.5 mm piece of PET in a manner similar to the method of Example 3. The lathe speed was set at 355 rpm (2.8 m/sec surface speed), the nozzle diameter was 0.125 mm, the nozzle pressure was 138 kPa, and the nozzle to substrate distance was 56 cm. The molten jet impinged the substrate at an angle of 45°. Under these conditions, the resulting lines were wavy and irregular, giving an overall random appearance to the resulting metal pattern. The nozzle was traversed longitudinally at a rate of 2.1 mm per revolution. Although the lines were only drawn in one direction, the resulting sample had continuous electrical continuity in all directions since adjacent lines intersected one another due to their waviness.

Example 7

A composite was made in a manner similar to Example 6 except that the nozzle to substrate distance was 58 cm, the impingement angle was 30°, the pressure was 90 kPa, and the transverse movement of the nozzle per revolution was 1.6 mm. The resulting composite is depicted in Fig. 7.

Example 8

A composite was made by drawing a set of parallel lines were drawn on a 30.5 cm by 30.5 cm by 0.25 mm piece of PETG in a manner similar to the method of Example 3. The lathe speed was 250 rpm (2 m/sec surface speed), the nozzle diameter was 0.08 mm, the nozzle pressure was 276 kPa, and the nozzle to substrate distance was 8 cm. Under these conditions, the resulting lines were wavy, with a rough wave amplitude of 1 mm and a rough wavelength of 3 mm. The nozzle was traversed longitudinally at a rate of 1 mm per revolution. Although the lines were only drawn in one direction, the resulting sample had continuous electrical continuity in all directions as the waviness resulted in intersection between adjacent lines.

Example 9

A composite was prepared as described in Example 8. A piece of smooth 0.005 mm polyimide was then placed against the side of the PETG having the metal lines and passed through a laminator with 15.4 cm diameter rolls heated to 138°C. The web rate through the rolls was 0.91 m/min and the sample was passed through the laminator 3 times. The result of this experiment was that the metal lines were pushed into the plastic so that the surface of the metal lines was flush with the PETG surface. The composite had superior resistance to scratching of the metal lines.

Example 10

A series of composites having a square mesh pattern as prepared in a manner similar to Example 3. The nozzle diameter was 0.06 mm, the nozzle pressure was 230 kPa, the nozzle to substrate distance was 5 mm, and the web speed was 2 m/sec. The metal was eutectic tin-bismuth. The resulting lines were 0.15 mm wide and 0.05 mm thick. The composites were tested for shielding capability, and the results are set forth in Table 1.

Table 1

Mesh (lines/cm)	Mesh (lines/inch)	EMI shielding dB at			
		30 MHz	100 MHz	300 MHz	1000 MHz
7.8	(20)	19	20	37	23
11.02	(28)	25	26	43	27
12.6	(32)	27	27	45	30
18.1	(46)	30	32	46	34
22.0	(56)	33	34	46	38
25.2	(64)	34	35	54	37
31.5	(80)	37	39	52	41
40.9	(104)	38	42	57	37
82.7	(210)(solid)	45	53	68	55

Example 11

A composite was made as follows: a roll of 20.5 cm wide by 0.05 mm thick PET was mounted on an inspection stand. This stand consists of an unwind roll and a windup roll spaced 0.61 m apart to allow convenient inspection of webs. A third roll was mounted in the stand so that the polymer film would pass against the third roll during a winding or unwinding operation. A stainless steel tube and nozzle similar to that described in Example 2 was positioned above the third roll, so that a polymer film would pass between the roll and the nozzle. The nozzle was positioned 2 mm from the film and at an angle of 45° from the film, measured between the metal jet and the longitudinal direction of approach of the film. The nozzle was also mounted on a transverse slide so that it could move freely from side to side, traversing the film. The takeup roll was driven by a variable speed motor so that the film could move at speeds of about 0 to 2 m/sec. The stainless steel tube and nozzle were heated and filled with molten indium at 200°C and the PET web was accelerated to 2 m/sec. The stainless steel tube and nozzle were heated and filled with molten indium at 200°C and the PET web was accelerated to 2 m/sec. A continuous line of indium metal was drawn on the PET. The nozzle was traversed back and forth to make a metal line in the form of a sine wave of 15.2 cm amplitude and 91 cm wavelength.

Example 12

A composite was made as follows: Using the procedures outlined in Examples 1 and 2, a set of parallel tin/bismuth metal lines was drawn onto a 30.5 cm by 0.05 mm piece of polyimide. The nozzle was the same hypodermic needle mounted in a stainless steel tube as was used in Example 2. A set of lines 3 mm apart was drawn onto the polyimide in one direction. A 30.5 cm by 30.5 cm by 0.25 mm piece of PET was then taped to the mandrel and a similar set of lines was drawn on the PET. The PET and the polyimide were placed against one another so that the lines of the polyimide were in contact with and intersected the lines of the PET at an angle of 90°. The PET and polyimide were then passed through a laminator in which the rolls were heated to 180°C. The metal lines on the polyimide melted and transferred to the PET to make a square mesh pattern on the PET. The metal lines were transferred because of the limited adhesion between the metal and the polyimide. The polyimide can be repeatedly reused for this purpose.

Example 13

A composite was made as follows: A set of parallel lines was drawn onto a 30.5 cm by 30.5 cm by 0.05 cm piece of polyimide following a procedure as in Example 12. In this case, however, two sets of lines intersecting at 90° were drawn onto the polyimide. The polyimide was then placed against a similar size piece of PET of 0.25 mm thickness so that the metal lines were in contact with the PET. The two pieces were then passed through a laminator as in Example 12. The square mesh pattern was transferred from the polyimide to the PET.

Example 14

A composite was made as follows: A set of parallel lines was drawn onto a 30.5 cm by 30.5 cm by 0.05 mm piece of polyimide in a manner similar to Example 12. Two 15.2 cm by 15.2 cm pieces were cut from this piece. A 15.2 cm by 15.2 cm by 0.25 mm cast PET film was placed against one of the polyimide pieces so that the metal lines were touching the polyimide. The two contacting pieces were then passed through the laminator, transferring the set of metal lines from the polyimide to the PET. The second 15.2 cm by 15.2 cm piece of polyimide was then placed against the piece of PET with the lines on the polyimide contacting and intersecting the lines on the polyester at 90°. These pieces were passed through the laminator again so that the lines from the polyimide were transferred to the PET, making a square mesh pattern on the PET.

Example 15

A set of parallel lines spaced 1 mm apart were drawn on two 30.5 cm by 30.5 cm pieces of cast PET. The PET pieces were placed against one another so that the metal lines were touching and intersecting at 90°. A sheet of 0.05 mm polyimide was placed on each side of the PET to keep the PET from sticking to the laminator rolls. It was then passed through the laminator which was set to 180°C and 0.91 m/min web speed. The two pieces of PET to be bonded to one another with a square mesh pattern of tin/bismuth sandwiched in between. The composite was then vacuum thermoformed in a manner similar to that used in Example 2, except the composite was heated for 30 seconds at 316°C.

Claims

1. A metal/polymer composite comprising a polymeric substrate and a discontinuous metal layer, said metal layer comprising a plurality of fine metal strands provided on said substrate, said metal strands individually having a cross-section with an area of 100 to 100,000 μm^2 and said cross-section having a flat portion and an arcuate portion.
2. The composite of claim 1 wherein the area of said cross-section is 100 to 10,000 μm^2 .
3. The composite of claim 1 wherein the area of said cross-section is 100 to 7500 μm^2 .
4. The composite of any preceding claim wherein said plurality of fine metal strands have a plurality of fused junctions.
5. The composite of any preceding claim wherein said composite is thermoformable, said metal strands having a melting point of less than the softening or melting temperature of said polymeric substrate.
6. The composite of any preceding claim wherein said metal layer is transparent and electrically conductive.
7. The composite of any preceding claim wherein said metal layer is in a mesh configuration.
8. The composite of claim 7 wherein said mesh comprises a plurality of regularly spaced horizontal strands and a plurality of regularly spaced vertical strands substantially perpendicular to said horizontal strands.
9. The composite of claim 8 wherein said vertical and horizontal strands are regularly spaced at an average spacing of between 2 and 200 strands per cm.
10. The composite of any one of claims 1-6 wherein said metal layer comprises a random, wandering configuration of the metal strands.
11. The composite of any preceding claim wherein said metal is a substantially pure metal or mixture of metals and is substantially undrawn.



12. The composite of claim 11 wherein said metal is selected from the group consisting of tin, lead, bismuth, zinc, indium, aluminum, and mixtures thereof.
- 5 13. The composite of any preceding claim wherein said polymer is a homopolymer or oligopolymer comprising monomers selected from the group consisting of polyesters, polyamides, polyimides, polyolefins, polyurethanes, polysulfones, polyethers, polycarbonates, cellulose esters, halogenated polyolefins, polyacetals, polystyrenes, and vinyl polymers.
- 10 14. The composite of claim 13 wherein said monomers are polyesters formed from terephthalic acid and one or more diols selected from the group consisting of ethylene glycol, propylene glycol, 1,4-butanediol, 1,6 hexanediol, and 1,4 cyclohexane dimethanol.
15. The composite of claim 2 wherein said composite is thermoformed.
16. The composite of claim 15 wherein said composite is stretched at least 50% during thermoforming.
17. The composite of claim 16 wherein said composite is stretched at least 200% during thermoforming.
- 20 18. The composite of claim 15 wherein said composite is stretched in certain regions at least 200% during thermoforming.
19. The composite of claim 11 wherein said metal layer blocks less than 5% of visible light transmitted therethrough.
- 25 20. A method of forming a metal/polymer composite comprising the steps of:
(a) providing a polymeric substrate, and
(b) squirting a plurality of fine molten metal strands onto said substrate wherein said metal strands individually have a cross-section with an area of 100 to 100,000 μm^2 and said cross-section has a flat portion and an arcuate portion.
- 30 21. The method of claim 20 wherein said composite is thermoformable, said metal having a melting point of less than the softening or melting temperature of said polymeric substrate.
- 35 22. The method of any one of preceding claims 20-21 wherein said metal layer is transparent and electrically conductive.
23. The method of claim 22 wherein said metal is a substantially pure metal or mixture of metals and is substantially undrawn.
- 40 24. The method of claim 23 further including the step of thermoforming said composite.
25. The method of claims 24 wherein said composite is stretched at least 50% during thermoforming.
26. The method of claim 25 wherein said composite is stretched at least 200% during thermoforming.
- 45 27. The method of claim 24 wherein said composite is stretched in certain regions at least 200% during thermoforming.
28. The process of claim 24 wherein the composite is shrunk by at least 25% during thermoforming.
- 50 29. The method of any one of preceding claims 20-28 further including transferring said metal layer to a second similar metal/polymer composite.
- 55 30. The method of any one of preceding claims 20-29 further including embedding said metal layer into said support surface so that said metal layer becomes substantially flush with said support surface.

**Patentansprüche**

- 5 1. Metall/Polymer-Verbundstoff, umfassend ein polymeres Substrat und eine zusammenhängende Metallschicht, wobei die Metallschicht eine Vielzahl feiner Metallstränge umfaßt, die auf dem Substrat vorgesehen werden, und wobei die Metallstränge einzeln einen Querschnitt mit einer Fläche von 100 ... 100.000 μm^2 haben und der Querschnitt einen flachen Abschnitt und einen gekrümmten Abschnitt aufweist.
- 10 2. Verbundstoff nach Anspruch 1, bei welchem die Fläche des Querschnitts 100 ... 10.000 μm^2 beträgt.
3. Verbundstoff nach Anspruch 1, bei welchem die Fläche des Querschnitts 100 ... 7.500 μm^2 beträgt.
- 15 4. Verbundstoff nach einem der vorgenannten Ansprüche, bei welchem die Vielzahl feiner Metallstränge eine Vielzahl verschmolzener Berührungsstellen aufweist.
5. Verbundstoff nach einem der vorgenannten Ansprüche, wobei der Verbundstoff warmformbar ist und die Metallstränge einen Schmelzpunkt unterhalb des Erweichungspunktes oder der Schmelztemperatur des polymeren Substrats haben.
- 20 6. Verbundstoff nach einem der vorgenannten Ansprüche, bei welchem die Metallschicht transparent und elektrisch leitfähig ist.
7. Verbundstoff nach einem der vorgenannten Ansprüche, bei welchem die Metallschicht eine Maschenkonfiguration aufweist.
- 25 8. Verbundstoff nach Anspruch 7, bei welchem die Masche eine Vielzahl regelmäßig beabstandeter horizontaler Stränge und eine Vielzahl regelmäßig beabstandeter vertikaler Stränge aufweist, die im wesentlichen zu den horizontalen Strängen senkrecht sind.
- 30 9. Verbundstoff nach Anspruch 8, bei welchem die vertikalen und horizontalen Stränge regelmäßig mit einem mittleren Abstand zwischen 2 und 200 Strängen pro cm beabstandet sind.
10. Verbundstoff nach einem der Ansprüche 1 bis 6, bei welchem die Metallschicht eine regellose, gewundene Konfiguration der Metallstränge aufweist.
- 35 11. Verbundstoff nach einem der vorgenannten Ansprüche, bei welchem das Metall ein im wesentlichen reines Metall oder eine Mischung von Metallen und im wesentlichen unverstreckt ist.
- 40 12. Verbundstoff nach Anspruch 11, bei welchem das Metall ausgewählt wird aus der Gruppe, bestehend aus Zinn, Blei, Bismut, Zink, Indium, Aluminium und deren Mischungen.
- 45 13. Verbundstoff nach einem der vorgenannten Ansprüche, bei welchem das Polymer ein Homopolymer oder Oligopolymer ist, umfassend Monomere, ausgewählt aus der Gruppe, bestehend aus Polyestern, Polyamiden, Polyimiden, Polyolefinen, Polyurethanen, Polysulfonen, Polyethern, Polycarbonaten, Celluloseestern, halogenierten Polyolefinen, Polyacetalen, Polystyrolen und Vinylpolymeren.
14. Verbundstoff nach Anspruch 13, bei welchem die Monomere Polyester sind, gebildet aus Terephthalsäure und einem oder mehreren Diolen, ausgewählt aus der Gruppe, bestehend aus Ethylenglykol, Propylenglykol, 1,4-Butandiol, 1,6-Hexandiol und 1,4-Cyclohexandimethanol.
- 50 15. Verbundstoff nach Anspruch 2, wobei der Verbundstoff warmgeformt wird.
16. Verbundstoff nach Anspruch 15, wobei der Verbundstoff während des Warmformens um mindestens 50 % verstreckt wird.
- 55 17. Verbundstoff nach Anspruch 16, wobei der Verbundstoff während des Warmformens um mindestens 200 % verstreckt wird.



18. Verbundstoff nach Anspruch 15, wobei der Verbundstoff in bestimmten Bereichen während des Warmformens um mindestens 200 % verstreckt wird.
19. Verbundstoff nach Anspruch 11, bei welchem die Metallschicht weniger als 5 % des durchgelassenen sichtbaren Lichts wegnimmt.
20. Verfahren zum Formen eines Metall/Polymer-Verbundstoffes, umfassend die Schritte:
 - (a) Bereitstellen eines polymeren Substrats und
 - (b) Spritzen einer Vielzahl feiner schmelzflüssiger Metallstränge auf das Substrat, wobei die Metallstränge einzeln einen Querschnitt von 100 ... 100.000 μm^2 haben und der Querschnitt einen flachen Abschnitt und einen gekrümmten Abschnitt hat.
21. Verfahren nach Anspruch 20, bei welchem der Verbundstoff warmformbar ist und das Metall einen Schmelzpunkt unterhalb des Erweichungspunktes oder der Schmelztemperatur des polymeren Substrats hat.
22. Verfahren nach Anspruch 20 und 21, bei welchem die Metallschicht transparent und elektrisch leitfähig ist.
23. Verfahren nach Anspruch 22, bei welchem das Metall ein im wesentlichen reines Metall oder eine Mischung von Metallen ist und im wesentlichen unverstreckt.
24. Verfahren nach Anspruch 23, ferner umfassend den Schritt des Warmformens des Verbundstoffes.
25. Verfahren nach Anspruch 24, bei welchem der Verbundstoff während des Warmformens um mindestens 50 % verstreckt wird.
26. Verfahren nach Anspruch 25, bei welchem der Verbundstoff während des Warmformens um mindestens 200 % verstreckt wird.
27. Verfahren nach Anspruch 24, bei welchem der Verbundstoff während des Warmformens in bestimmten Bereichen um mindestens 200 % verstreckt wird.
28. Verfahren nach Anspruch 24, bei welchem der Verbundstoff während des Warmformens um mindestens 25 % geschrumpft wird.
29. Verfahren nach einem der Ansprüche 20 bis 28, ferner einschließlich des Transferierens der Metallschicht auf einen zweiten, ähnlichen Metall/Polymer-Verbundstoff.
30. Verfahren nach einem der Ansprüche 20 bis 29, ferner einschließlich des Einbetten der Metallschicht in die Trägeroberfläche, so daß die Metallschicht mit der Trägeroberfläche weitgehend fluchtet.

Revendications

1. Composite de métal/polymère comprenant un substrat polymérique et une couche métallique discontinue, la couche métallique comprenant une pluralité de fins brins métalliques amenés sur ledit substrat, les brins métalliques ayant individuellement une coupe transversale d'une aire de 100 à 100.000 μm^2 et la coupe transversale comportant une partie plane et une partie arquée.
2. Composite suivant la revendication 1, dans lequel l'aire de la coupe transversale est de 100 à 10.000 μm^2 .
3. Composite suivant la revendication 1, dans lequel l'aire de la coupe transversale est de 100 à 7.500 μm^2 .
4. Composite suivant l'une quelconque des revendications précédentes, dans lequel la pluralité de fins brins métalliques comporte une pluralité de jonctions soudées.



5. Composite suivant l'une quelconque des revendications précédentes, dans lequel le composite est thermoformable, les brins métalliques ayant un point de fusion inférieur à la température de ramollissement ou de fusion du substrat polymérique.
- 5 6. Composite suivant l'une quelconque des revendications précédentes, dans lequel la couche métallique est transparente et électriquement conductrice.
7. Composite suivant l'une quelconque des revendications précédentes, dans lequel la couche métallique est dans une configuration maillée.
- 10 8. Composite suivant la revendication 7, dans lequel les mailles comprennent une pluralité de brins horizontaux régulièrement espacés et une pluralité de brins verticaux régulièrement espacés sensiblement perpendiculaires aux brins horizontaux susdits.
- 15 9. Composite suivant la revendication 8, dans lequel les brins verticaux et horizontaux sont régulièrement espacés à un espacement moyen entre 2 et 200 brins par centimètre.
10. Composite suivant l'une quelconque des revendications 1 à 6, dans lequel la couche métallique comprend une configuration migratrice, désordonnée des brins métalliques.
- 20 11. Composite suivant l'une quelconque des revendications précédentes, dans lequel le métal est un métal ou mélange de métaux essentiellement pur et est essentiellement non étiré.
- 25 12. Composite suivant la revendication 11, dans lequel le métal est choisi dans le groupe comprenant l'étain, le plomb, le bismuth, le zinc, l'indium, l'aluminium et leurs mélanges.
- 30 13. Composite suivant l'une quelconque des revendications précédentes, dans lequel le polymère est un homopolymère ou oligopolymère comprenant des monomères choisis dans le groupe comprenant les polyesters, les polyamides, les polyimides, les polyoléfines, les polyuréthanes, les polysulfones, les polyéthers, les polycarbonates, les esters cellulosiques, les polyoléfines halogénées, les polyacétals, les polystyrènes et les polymères vinyliques.
- 35 14. Composite suivant la revendication 13, dans lequel les monomères sont des polyesters formés à partir d'acide téréphtalique et d'un ou plusieurs diols choisis dans le groupe comprenant l'éthylène glycol, le propylène glycol, le 1,4-butanediol, le 1,6-hexanediol et le 1,4-cyclohexane diméthanol.
15. Composite suivant la revendication 2, dans lequel ledit composite est thermoformé.
- 40 16. Composite suivant la revendication 15, dans lequel ledit composite est étiré d'au moins 50 % au cours du thermoformage.
17. Composite suivant la revendication 16, dans lequel ledit composite est étiré d'au moins 200 % au cours du thermoformage.
- 45 18. Composite suivant la revendication 15, dans lequel ledit composite est étiré dans certaines zones d'au moins 200 % au cours du thermoformage.
19. Composite suivant la revendication 11, dans lequel la couche métallique arrête moins de 5 % de la lumière visible transmise à travers celui-ci.
- 50 20. Procédé de formation d'un composite de métal/polymère comprenant les étapes suivantes :
- (a) la formation d'un substrat polymérique, et
- (b) l'injection d'une pluralité de fins brins métalliques fondus sur le substrat, les brins métalliques susdits ayant individuellement une coupe transversale d'une aire de 100 à 100.000 μm^2 et la section transversale comportant une partie plane et une partie arquée.
- 55 21. Procédé suivant la revendication 20, dans lequel le composite est thermoformable, le métal ayant un point de fusion inférieur à la température de ramollissement ou de fusion du substrat polymérique.



22. Procédé suivant l'une ou l'autre des revendications 20 et 21, dans lequel la couche métallique est transparente et électriquement conductrice.
- 5 23. Procédé suivant la revendication 22, dans lequel le métal est un métal ou mélange de métaux essentiellement pur et est essentiellement non étiré.
24. Procédé suivant la revendication 23, comprenant de plus l'étape de thermoformage du composite.
- 10 25. Procédé suivant la revendication 24, dans lequel le composite est étiré d'au moins 50 % au cours du thermoformage.
26. Procédé suivant la revendication 25, dans lequel le composite est étiré d'au moins 200 % au cours du thermoformage.
- 15 27. Procédé suivant la revendication 24, dans lequel le composite est étiré dans certaines zones d'au moins 200 % au cours du thermoformage.
28. Procédé suivant la revendication 24, dans lequel le composite subit un retrait d'au moins 25 % au cours du thermoformage.
- 20 29. Procédé suivant l'une quelconque des revendications 20 à 28, comprenant de plus le transfert de la couche métallique sur un second composite de métal/polymère similaire.
- 25 30. Procédé suivant l'une quelconque des revendications 20 à 29, comprenant de plus l'incorporation de la couche métallique dans la surface de support de telle sorte que la couche métallique vienne sensiblement au niveau de la surface de support.

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