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Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

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(54) **Folyáshatárral rendelkező polimerkeverék és alkalmazása fém-polimer kompozitok előállítására**

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Blend of polymers having yield stress and use thereof for the manufacture of metal-polymer composites

The present invention relates to novel polymer blends having yield stress and to the use thereof for the manufacture of metal-polymer composites.

[Background of the invention]

One of the ways being explored for cutting automotive fuel consumption is reducing vehicle weight. In this context, research is actively being carried out into replacing metal sheets with metal-polymer composites, such as metal-polymer-metal structures, also known as sandwich structures, or metal facings covered with polymer.

The polymers used for these composites must fulfil many requirements, and in particular exhibit adhesion to the metal and have high rigidity and elongation greater than that of the metal.

In order to enable a substantial reduction in weight, the polymer must be of quite a considerable thickness, typically from 300 µm up to a number of mm. It is therefore preferable to use an extrudable thermoplastic polymer rather than a thermosetting polymer which has to be applied in solution.

The polymer used should furthermore be compatible with the cataphoresis step used in the automotive sector for painting. This method involves curing at a temperature of as high as 210°C for approximately 45 minutes. When the polymer becomes too fluid, it yields and causes slippage of the metal sheets, so destroying the composite.

Patent application WO 2005/014270 proposes sandwich structures comprising a blend of polyamide 6, modified polyethylene and styrene-maleic anhydride (SMA) copolymer as the polymer. Said blend exhibits satisfactory properties, but its high melting point (220°C), and hence its high processing temperature (240°C), makes it incompatible with certain pieces of equipment used for roll bonding assembly. This is because these pieces of equipment are incapable of achieving the temperatures in excess of 220°C which are required to melt this polymer blend at the surface in order to allow the polymer blend to spread out on the metal and to take adhesion to the metal to completion. Furthermore,

it has proven difficult to ensure a uniform distribution of the styrene-maleic anhydride (SMA) copolymer in the blend, which has an impact on the uniformity of the morphology and the adhesion of the film.

[Technical problem]

There is accordingly a need for a polymer blend having the characteristics required for the manufacture of metal-polymer composites which does not exhibit the above-mentioned drawbacks. In particular, there is a need for a polymer blend of a simple formulation which is capable of withstanding the cataphoresis step at 210°C while still having a melting temperature which does not exceed 210°C.

[Summary of the invention]

The invention arises from the idea of using a polymer blend which behaves as a yield stress fluid, i.e. which, even in the molten state, has sufficient creep resistance to withstand the cataphoresis step.

A thorough investigation has revealed blends of polyamide and modified polyethylene which have the required applicational properties with regard to adhesion, rigidity and elongation and which, in the molten state, are yield stress fluids.

Thus, according to a first aspect, the invention relates to a biphasic polymer blend, comprising:
(a) a polyamide having a melting point of at most equal to 210°C,
(b) a modified polyolefin comprising carboxylic functions,
the rheological behaviour of which in the molten state is characterised by a yield stress of at least 50 Pa.

The polymer blend according to the invention preferably comprises 30 to 70% by weight of polyamide. The polymer blend furthermore advantageously comprises 30 to 70% by weight of modified polyolefin.

The modified polyolefin is preferably a modified polyethylene. Advantageously, it is a maleic anhydride-modified polyolefin. A polyolefin modified by 0.01 to 20% by weight of a compound comprising carboxylic functions is particularly preferred.

The polyamide is advantageously a polyamide 11.

According to one preferred embodiment, the polymer blend according to the invention comprises a continuous phase, also known as the matrix, essentially composed of polyamide and a co-continuous or disperse phase essentially composed of polyolefin. When the phase is dispersed, it preferably assumes the form of nodules, the average diameter of which is preferably less than 500 nm. When the blend is made up solely of these two polymers, the polymer blend thus takes the form of a polyamide matrix in which the modified polyolefin is dispersed or forms a co-continuous phase.

Advantageously, the blend according to the invention furthermore comprises 5 to 20% by weight of fillers.

The blend according to the invention preferably has a yield stress of between 200 and 2000 Pa.

According to another aspect, the invention relates to a method for preparing the above-described polymer blend comprising the steps of:
(a) providing an appropriate quantity of polyamide and an appropriate quantity of modified polyolefin comprising carboxylic functions; and
(b) blending the polyamide and the modified polyolefin at a temperature greater than the melting peak of the polyamide.

According to still another aspect, the invention relates to a method for manufacturing a metal-polymer composite comprising the steps consisting of:
(i) providing a first metal sheet, optionally heated to the melting temperature of the polymer blend;
(ii) applying a polymer blend according to the invention onto the first metal sheet to form a metal-polymer composite;
(iii) if appropriate, applying a second metal sheet optionally heated to the melting temperature of the polymer onto the polymer blend to form a metal-polymer-metal composite; and
(iv) heating the composite until the polymer blend in contact with the metal melts to take adhesion to completion.

Also, according to another aspect, the invention relates to the sandwich structures comprising between two metal sheets a film of the polymer blend according to the invention together with facings comprising a metal sheet coated with the polymer blend according to the invention.

Finally, according to a final aspect, the invention relates to a facing comprising a metal sheet coated with the polymer blend according to the invention.

[Definitions]

In the context of present description, the term "yield stress fluid" is taken to mean a rheological behaviour of a deformable material which is characterised in that flow only takes place beyond a certain stress value, known as the yield stress. The notion of yield stress is known for fluids in general and for polymers in the molten state in particular.

Furthermore, the term "creep resistance" is taken to mean the absence of a rate of deformation, for example by flow, of a material subjected to a stress for a sufficient duration.

The term "polymer blend" is taken to mean a composition of a plurality of, in particular two, immiscible polymers. Polymers are for the most part mutually immiscible due to their high molar masses and/or unfavourable interactions. Polymer blends therefore most frequently take the form of multiphase structures. In the case of a blend of two polymers, biphasic blends may comprise a continuous phase and a dispersed phase. Most frequently, the majority polymer forms the continuous phase while the minority polymer forms the dispersed phase. When the polymers are present in similar proportions, blends in which the two phases are both continuous or "co-continuous" may also be observed. There are various types of morphology in polymer blends, in particular the nodular morphology, the fibrillar morphology and the lamellar morphology.

In principle, the blend described in the present application is a physical blend which does not involve any covalent bonds between the constituents. However, at the interface of the polymers, the terminal amino groups of the polyamide may form imide bonds with the carboxylic groups of the modified polyolefin, as will discussed in greater detail below.

The term "modified polyolefin" is taken to denote a polyolefin comprising polar and in particular carboxylic groups. These groups may have been introduced into the polyolefin during or subsequently to polymerisation. The resultant structural units may therefore be located in the main chain or in the side chains of the modified polymer. In practice, modified

polyolefins are obtained by copolymerising an olefin in the presence of appropriate monomers or by reacting the polyolefin with appropriate compounds, this also being known as grafting. Unsaturated carboxylic acids and the derivatives thereof, in particular the anhydrides thereof, are appropriate monomers and/or compounds which are preferred for the purposes of the present invention.

The term "grafting rate" used hereafter is taken to mean the concentration by mass of compound used to modify the polyolefin in the modified polyolefin, based on the final weight of the modified polyolefin. Unless indicated otherwise, said rate denotes the overall concentration by mass in the polymer, without distinguishing whether it is present in the polymer or in monomer form.

[Components of the blend]

The described polymer blend comprises at least two constituents, namely a polyamide and a modified polyolefin.

In certain applications, it may be worthwhile adding other constituents, for example, as will be explained below, inorganic fillers capable of still further increasing the yield stress of the blend.

However, in order to avoid any problems of incompatibility and/or homogeneity, the blend is preferably made up of polyamide and grafted polyolefin and contains no other polymer. It preferably also contains no other compound capable of reacting with the constituents of the blend or of reacting in a moist environment resulting in a deterioration in the adhesion or stability of the blend.

Without wishing to be tied to any particular theory, it is assumed that the yield stress fluid behaviour is associated with the presence of a three-dimensional structure. Thanks to this structure, the fluid is capable of resisting a stress of less than τ_0. When the stress exceeds τ_0, the three-dimensional structure is destroyed and the polymer yields.

In the described polymer blend, di-block copolymers are formed by reaction between the terminal amino groups of the polyamide and the carboxylic functions of the modified reactive groups on the polyolefin. The scheme of Figure 1 illustrates the reaction at the interface of the polymers.

The copolymers formed *in situ* in this manner at the interfaces of the blend may perform the role of a compatibilising agent, so enabling better dispersion of the two phases and, possibly, smaller nodules closer to one another. The small internodular distance enables interaction between the copolymer chains of neighbouring nodules by physical entangling, forming a three-dimensional rubbery network (see Figure 2). This three-dimensional network formed by internodular interaction limits deformation under stress until it disappears at a stress known as the yield stress.

Polyamides are polymers containing amide functions (-C(=O)-NH-) and may be obtained by:

(1) ring-opening polymerisation of lactams; or

(2) polycondensation of amino acids; or

(3) polycondensation of diamines with diacids.

Aliphatic polyamides are designated by one or more figures denoting the number of carbon atoms present in the structural repeat unit. PA 6 or PA 11 is thus obtained by polycondensing an amino acid or a lactam respectively having 6 or 11 carbon atoms in the structural unit. In designations of the type PA 6-6, the values correspond to the number of carbon atoms in the diamine and in the diacid. Polyamides may be aliphatic, semi-aromatic (only one of the monomers is aromatic) or aromatic. Homopolymers formed from a single monomer are preferred, but polyamide copolymers obtained from a plurality of different monomers may also be considered.

Semi-crystalline polyamides are preferred over amorphous polyamides since, having a melting peak rather than a single softening point, they are more readily processed.

For the intended application, the melting point of the polyamide is advantageously between 160 and 210°C. According to one particular embodiment, the melting point of the polyamide is between 170 and 200°C.

Polyamides suitable for the described blend which may be mentioned in particular include polyamide 11 having a melting point of between 177 and 190°C, or alternatively polyamide 12 having a melting point of between 172 and 180°C.

The molar mass of the polyamide has an impact on the properties of the blend since it determines the number of terminal amino groups available

to form the copolymer in contact with the carboxylic functions of the modified polyolefin. Molar mass furthermore influences melting temperature. The molar mass of the polyamide is preferably between 1000 and 100,000, advantageously between 10,000 and 30,000 g/mol.

In practice, the melt index of the polyamide is preferably between 1 and 40, preferably 10 to 25 cm^3/10 min under 2.16 kg at 235°C.

Commercially available polyamides frequently comprise 5 to 20% by weight, preferably 10 to 20% by weight, of plasticisers. Addition of a plasticiser may contribute to improving impact resistance. Appropriate plasticisers which may be mentioned are ε-caprolactam, N-butylbenzenesulfonamide or cetyl para-oxybenzoate.

However, as previously mentioned, the polymer blend according to the invention preferably does not comprise any additives other than those which may be present in the commercial polymers used and the inorganic fillers discussed below.

The Newtonian viscosity of the polymers, and more specifically the ratio of the viscosities of the two base constituents, is also an important factor for obtaining a blend with satisfactory properties. This is because the viscosities have an influence on the morphology of the blend. A rule of thumb recommends a ratio between the shear viscosity of the modified polyolefin and that of the polyamide of between 1 and 10. The Newtonian viscosity of the polyamide is preferably between 500 and 5000, preferably 1000 to 4000 Pa·s at 210°C.

The blend according to the invention generally comprises between 30 and 70% by weight, and more preferably between 40 and 65% by weight, of polyamide. Below 30%, the proportion of polyamide is generally insufficient to impart the advantageous mechanical properties of polyamide to the blend, while above 70%, the risk arises of there no longer being sufficient modified polyolefin to promote *in situ* compatibilisation of the two constituents.

The modified polyolefin present in the blend may be obtained starting from a thermoplastic polyolefin. The polyolefin may in particular be selected from polyethylene, polypropylene, polymethylpentene and polybutene. A polymer having appropriate properties in terms of rigidity, density and crystallinity will be selected from these families.

The particularly preferred polyolefin is polyethylene and may be a homopolymer such as HDPE (high-density polyethylene) or LDPE (low-density polyethylene) or LLDPE (linear low-density polyethylene) or copolymers derived from polyethylene such as ethylene and octene copolymers.

In order to permit *in situ* compatibilisation at the interfaces in the blend, the polyolefin is modified with groups comprising carboxylic functions. These groups may be introduced during polymerisation, by copolymerisation in the presence of appropriate monomers, or by grafting subsequently to polymerisation.

These groups comprising carboxylic functions are in particular carboxylic acid groups or derivatives such as, for example unsaturated acids comprising 1 to 6 carboxylic functions such as maleic acid, fumaric acid, mesaconic acid, citraconic acid, aconitric acid and itaconic acid, 5-norbornene-2,3-dicarboxylic acid, 1,2,3,6-tetrahydrophthalic acid, acrylic acid and methacrylic acid together with the corresponding anhydrides, salts and esters. The polyolefin is preferably modified with maleic anhydride.

Numerous modified polyolefins comprising carboxylic functions are commercially available.

The melt index of the modified polyolefin is preferably between 0.1 and 30, preferably between 0.2 and 10 and most particularly between 0.2 and 2 cm^3/10 min under 5 kg at 190°C in order to facilitate blending thereof with the polyamide.

The modified polyolefins may assume ionomer form, for example following at least partial neutralisation of the carboxylic functions.

The polyolefin grafting rate is an important parameter since it can influence yield stress by affecting the number of bonds capable of forming at the interface. Generally, it is sufficient for the polyolefin grafting rate is between 0.01 and 20%, preferably between 0.02 and 10% and in particular between 0.03 and 5% by weight of carboxylic acid or the derivative thereof based on the weight of the polyolefin.

The Newtonian viscosity of the modified polyolefin is preferably greater than 5000, and in particular at least 20,000 Pa·s at 220°C. Viscosity may, however, be difficult to determine when the modified polyolefin exhibits viscoelastic behaviour of the resilient solid type.

The blend according to the invention generally comprises between 30 and 70% by weight, and more preferably between 35 and 60% by weight, of modified polyolefin.

The yield stress of the polymer blends according to the invention may be further increased by adding inorganic fillers.

The quantity of fillers necessary to bring about a yield stress is higher for spherical fillers which do not interact with one another than for structuring fillers.

Structuring fillers are taken to mean elemental nanoscale particles which form microscale aggregates and which, above a certain concentration, form a network of fillers (phenomenon of percolation). These fillers may be spherical, like nanostructured silicas, or have a high form factor, i.e. greater than 100, like carbon nanotubes and exfoliated clays, the form factor being defined as the ratio of the largest dimension of the particle to the thickness thereof.

By addition of fillers, the desired yield stress is retained while increasing the quantity of polyamide.

Certain fillers are of particular interest because they furthermore make it possible to impart one or more supplemental functionalities to the blend. Adding carbon fillers in various forms (carbon black, carbon fibres, graphite, carbon nanotubes) for instance makes it possible to make the polymer blend conductive, which is of interest for certain painting processes (see "Conductive polyphenylene ether/polyamide blends for electrostatic painting applications" J.J. Scobbo, Antec'98, pp. 2468-2472). It may therefore be advantageous to add conductive fillers to the polymer blend.

In order to safeguard the properties of the polymer blend, in particular a low viscosity, it is preferable to keep the proportion of fillers to within a reasonable value.

The proportion of fillers in the polymer blend according to the invention may range from 0 to 30% by weight, and more particularly from 5 to 20% by weight, of the complete blend.

[Preparation and properties of the blend]

The described polymer blend is prepared in the simplest manner by intimately blending the constituents at a temperature at which the polymer components are in the molten state. Intimate blending may proceed by various *per se* known means, for example in a Haake type internal reactor or a twin-screw extruder.

In the molten state, the polymer blends to which the present invention relates behave as yield stress fluids, i.e. they only flow when the stress applied exceeds a certain threshold.

Investigation of the complex shear modulus ($G^*(\omega)=G'(\omega)+jG''(\omega)$) of these blends reveals a plateau in the elastic modulus G' at low frequencies, i.e. of less than 1 rad/s. As mentioned above, this phenomenon may be explained by the formation of an *in situ* copolymer at the interface between the polyamide and the modified polyolefin.

The yield stress value measured by the method described below is at least 50 Pa, which approximately corresponds to the stress exerted by the weight of a 0.8 mm thick metal facing in a sandwich structure. Advantageously, the yield stress of the blends is between 200 and 2000 Pa.

Since the described polymer blend only yields when the stress exceeds the yield stress, it is capable of meeting the apparently irreconcilable conditions set by the thermal capacity of the rolling units and cataphoresis resistance.

As mentioned above, the morphology of polymer blend is preferably a continuous phase forming the matrix for a dispersed phase or a co-continuous phase. When the blend comprises a dispersed phase, the dispersed phase is most frequently observed to assume nodule form. The dispersed phase may nevertheless also form fibres (fibrillar morphology) or layers (lamellar morphology).

A nodular morphology is however preferred. This is because such a morphology provides an extensive polymer interface and consequently ensures the formation of a large network of bonds at the interface, so ensuring an elevated yield stress. Preferably, average nodule diameter as determined experimentally by scanning electron microscopy (SEM) and image

analysis is less than 500 nm, preferably less than 300 nm, in order to promote interaction between the polymer chains to form a rubbery network which brings about the yield stress.

The polyamide and polyolefin are compatibilised by the *in situ* formation of copolymers formed by reaction between the terminal amino groups of the polyamides and the carboxylic functions of the modified polyolefin.

The continuous phase forming the matrix is preferably essentially composed of the polyamide while the dispersed or co-continuous phase is composed of the modified polyolefin. Such a morphology of the polymer blend provides the advantage of imparting the advantageous mechanical properties of the polyamide to the polymer blend.

In principle, it is preferred for the number of copolymers per unit of surface area of the interface to be high, resulting a maximum yield stress. However, an excessive concentration of copolymers at the interface may affect other properties such as viscosity. Accordingly, a number of copolymers of preferably between 3 and 50% will advantageously be sought, this percentage corresponding to a reaction yield per unit mass based on the limiting species. Beyond 50%, the polymer blends obtained have properties which differ from those sought.

(Applications)

By virtue of the above-mentioned properties, the described polymer blends are particularly useful for manufacturing metal-polymer composites, such as sandwich structures or metal facings covered with polymer. Such composites are particularly sought after in the automotive industry.

The composites are most frequently made up of a film of polymer blend according to the invention applied to one sheet or between two metal sheets.

The metal is most frequently a steel, the specific grade of which will be selected on the basis of the intended application. In the automotive field, the grades of steel normally used are thus ES (EN DC01 to DC06) and HLE (EN HZ40 LA to H400 LA). The thickness of the metal sheets used for this application will generally be between 0.1 mm and 3 mm. The metal may be untreated but most frequently will be provided with one or more coatings in order to improve its properties, such as for example a

coating of zinc or zinc alloy applied by galvanisation or electrodeposition, or a surface treatment, a primer, a base coat of paint or lacquer or alternatively a layer of oil.

The metal-polymer composites may be manufactured according to any per se known method.

According to another aspect, the invention thus relates to a method for manufacturing a metal-polymer composite comprising the steps consisting of:

a. providing a first metal sheet, optionally heated to the melting temperature of the polymer;

b. applying a polymer blend according to the invention onto the first metal sheet to form a metal-polymer composite;

c. if appropriate, applying a second metal sheet optionally heated to the melting temperature of the polymer onto the polymer blend to form a metal-polymer-metal composite; and

d. heating the composite until the polymer blend in contact with the metal melts to take adhesion to completion.

The polymer blend is preferably extruded beforehand to form a polymer film. It is, however, also possible to extrude the polymer film directly onto the first metal sheet or to roll bond the polymer film between the two metal sheets in a single step.

Extrusion is preferably performed in a co-rotating twin-screw extruder. The thickness of the polymer film depends on the application and is preferably between 0.05 and 5 mm, and more preferably between 0.2 and 1 mm.

The described polymer blend makes it possible to obtain a polymer surface which adheres to products such as sealants, structural adhesives and crash adhesives. The polymer surface of the metal-polymer composites obtained can thus be overmoulded with polymer.

According to another aspect, the invention relates to the multilayer structures comprising a film of the polymer blend as described above between two metal sheets, in particular metal-polymer-metal composites, such as sandwich structures, together with facings comprising a metal sheet coated with the polymer blend according to the invention. These products are light in weight, rigid, deep drawable and inexpensive,

withstand cataphoresis and are consequently particularly useful in the automotive industry. Depending on the application, sandwich structures having two facings of a different nature and/or thickness may be used.

The invention will be described in greater detail by means of the following examples and the appended drawings, in which:

Fig. 1: shows a reaction scheme between the functional groups of the polymers at the interface of a polymer blend according to the invention;

Fig. 2: is a schematic representation of the interaction between modified polyolefin nodules forming a three-dimensional network;

Fig. 3: shows scanning electron microscopy (SEM) micrographs of the blends of Examples 1 to 7 after extraction of the polyolefin phase;

Fig. 4: is a graph plotting deformation rate dE/dt against stress σ of the blends of Examples 1 to 4;

Fig. 5: is a graph plotting deformation rate dE/dt against stress σ of the blends of Examples 5 to 7;

Fig. 6: is a graph of elastic modulus G' for different frequencies of the blends of Examples 1-4;

Fig. 7: is a graph of elastic modulus G' for different frequencies of the blends of Examples 5 to 7;

Fig. 8: is a diagram of the experimental setup for evaluating the cataphoresis resistance of a sandwich (DP 500 steel, thickness=0.8 mm and polymer blend thickness=1 mm); and

Fig. 9: shows adhesion evaluated by dolly testing for the blends of Examples 1-4.

EXAMPLES

EXAMPLE 1 (PA 11/POE-MAH)

After prior drying in an oven under a vacuum at 70°C, 60 g of polyamide 11 from Arkema (PA 11 Rilsan®) and 40 g of polyethylene-octene copolymer modified with 1.5% maleic anhydride (POE-MAH, Tabond 8010 available from Silon International) were introduced into a Haake Rheomix 600 internal mixer adjusted to a temperature of 210°C (20°C higher than the melting temperature of the polyamide).

The blend was kneaded for between 5 and 10 minutes until the torsional torque exerted on the mixer blades stabilised.

The resultant polymer blend was then pressed in a Lescuyer 200 bar hydraulic press to make 1 mm thick films.

Examination by scanning electron microscope after extraction of the modified polyolefin with toluene at 110°C for 2 to 7 days revealed that the biphasic blend comprised a continuous phase and nodules of modified polyolefin with a diameter of the order of 300 nm (see Figure 3).

EXAMPLES 2-4 (PA 11/POE-MAH)

In order to evaluate the impact of the proportion of polyamide and polyolefin in the blend, the procedure set out in the previous example was repeated, but with the proportions of the polymers being varied as shown in Table 1 below.

Examination by scanning electron microscope after extraction of the modified polyolefin as described in the previous example revealed (see Figure 3) that the blend was biphasic for all the examples and that, for Examples 1 and 2, it comprised nodules of modified polyolefin with a diameter of the order of 300 nm and, for Examples 3 and 4, an appearance at the limit of co-continuity.

EXAMPLE 5 (PA 11/PE-MA$^-$Na$^+$)

After prior drying in an oven under a vacuum at 80°C, 60 g of polyamide 11 from Arkema (PA 11 Rilsan®) and 40 g of partially neutralised (sodium counter-ion) low-density polyethylene modified with 0.5% by weight of maleic anhydride (Priex® 35392 ionomer available from Addcomp Holland BV) were introduced into a Haake Rheomix 600 internal mixer adjusted to a temperature of 210°C (20°C higher than the melting temperature of the polyamide).

The blend was kneaded for between 5 and 10 minutes until the torsional torque exerted on the mixer blades stabilised.

The resultant polymer blend was then pressed in a Lescuyer 200 bar hydraulic press to make 1 mm thick films.

Examination by scanning electron microscope after extraction of the modified polyolefin with toluene as described in Example 1 revealed that

the blend was biphasic and comprised a continuous phase and nodules of modified polyolefin with a diameter of the order of 170 nm.

EXAMPLE 6 (PA 11/POE-MAH/Si)

In order to investigate the effect of an inorganic filler on yield stress, a polymer blend furthermore containing a silica as filler was prepared.

More specifically, a polymer blend was prepared according to the procedure stated in Example 1 using 49.5 g of a polyamide 11 (PA 11 Rilsan® available from Arkema) as the polyamide and 40.5 g of polyethylene octene modified with 1.5% maleic anhydride (POE-MAH, Tabond 8010 available from Silon International) as the modified polyolefin together with 10 g of hydrophilic pyrogenic silica with a specific surface area of approximately 200 m^2/g (Wacker fumed silica HDK N 20). This blend had a polyamide/polyolefin ratio equivalent to the blend of Example 2 (55% PA 11 and 45% POE-MAH).

Examination by scanning electron microscope after extraction of the modified polyolefin as described in Example 1 revealed that the blend was biphasic and comprised a continuous phase and nodules of modified polyolefin with a diameter of the order of 300 nm (see Figure 3).

EXAMPLE 7 (PA 11/PE-MA$^-$Na$^+$)

After prior drying in an oven under a vacuum at 80°C, 60 g of polyamide 11 from Arkema (PA 11 Rilsan®) and 40 g of partially neutralised (sodium counter-ion) high-density polyethylene modified with 0.05% by weight of maleic anhydride (Prlex® 3310l ionomer available from Addcomp Holland BV) were introduced into a Haake Rheomix 600 internal mixer adjusted to a temperature of 210°C (20°C higher than the melting temperature of the polyamide).

The blend was kneaded for between 5 and 10 minutes until the torsional torque exerted on the mixer blades stabilised.

The resultant polymer blend was then pressed in a Lescuyer 200 bar hydraulic press to make 1 mm thick films.

Examination by scanning electron microscope after extraction of the modified polyolefin with toluene as described in Example 1 revealed that the blend was biphasic and comprised a continuous phase and nodules of modified polyolefin with a diameter of the order of 200 to 250 nm.

Table 1: Composition of the polymer blends

Example	Polyamide		Modified polyolefin		Silica
	Type	Proportion (% by weight)	Type	Proportion (% by weight)	Proportion (% by weight)
1	PA 11	60	POE-MAH	40	-
2	PA 11	55	POE-MAH	45	-
3	PA 11	50	POE-MAH	50	-
4	PA 11	45	POE-MAH	55	-
5	PA 11	60	PE-MAH ionomer (0.5%)	40	-
6	PA 11	49.5	POE-MAH	40.5	10
7	PA 11	60	PE-MAH ionomer (0.05%)	40	-

EVALUATION OF THE POLYMER BLENDS

A. Yield stress

Rheological measurements were carried out on an imposed-stress rheometer using cone-plate geometry (Rheometrics Scientific SR5).

The polymer blend sample was prepared in the form of a sheet 1 mm in thickness and 25 mm in diameter. This sample was exposed to an instantaneous stress which varied between 0 and 5000 Pa. The change in deformation was monitored by a displacement sensor. The measurement temperature depended on the polymer forming the matrix and was identical to the blending temperature (20°C above the melting peak of the polyamide).

Yield stress was determined from a graph in which the deformation rate was plotted against stress. When the curve formed a threshold, the molten

blend behaved as a yield stress fluid. The yield stress was determined from the graph curve as the stress limit beyond which the deformation rate increased.

It will be noted that all the blends of Examples 1 to 7 exhibited a yield stress at the temperature under consideration. The results are illustrated in detail in Figures 4 and 5. The yield stress values determined from the curves are shown in Table 2 below.

Table 2: Yield stress of the polymer blends

Example	**Yield stress** [Pa]
1	50
2	200
3	200
4	700
5	400
6	2000
7	200

The progressive increase in yield stress observed for Examples 1 to 4 from 50 Pa to 700 Pa may be explained by an increase in nodule density, given that the diameters thereof were unchanged, and consequent strengthening of the interactions between nodules and chain entanglement phenomena, which in turn resulted in slower chain relaxation and the appearance of a rubbery plateau.

It will furthermore be noted that the presence of ionic groups would appear to have a favourable effect with regard to yield stress.

Finally, the addition of inorganic fillers had a significant effect on the yield stress of the blends according to the invention, enabling an increase from 200 Pa for Example 2 to 2000 Pa for Example 6.

8. Elastic modulus

The complex shear modulus was determined on an RMS 800 imposed-deformation rheometer using plate-plate geometry over a frequency range of 0.01-100 rad/s, the sample having previously been converted into a

sheet 1 mm in thickness and 25 mm in diameter, the measurement temperature being identical to the blending temperature (20°C above melting peak of the polyamide).

This technique permitted an investigation of viscoelasticity in the linear range of the polymer in the molten state. In qualitative terms, the existence of a yield stress correlated to the observation of a plateau at low frequencies on the curve plotting elastic modulus G' against loading frequency. In this zone, the material behaved like a rubber, the crosslinks points being replaced by strong interactions of the physical entanglement type.

The results are illustrated in Figures 6 and 7.

Figure 6 illustrates the shape of the resultant curve. The blend of Example 1 had a low elastic modulus at low frequencies, the plateau of which was not visible because it was located outside the investigated range. Increasing the proportion of modified polyolefin in the formulation from 40% to 55% by weight brought about a progressive increase in elastic modulus and the appearance of a plateau around 10,000 Pa at low frequency.

Figure 7 shows the curve obtained for the blends according to Examples 5, 6 and 7. It will be noted that the elastic modulus had a plateau at low frequencies for all these blends. Furthermore, the addition of fillers was observed to have a major impact with regard to elastic modulus. This is because adding fillers made it possible to adjust the elastic modulus value of the blend of Example 6 (polyamide/polyolefin mass ratio 55:45, as in Example 2) back down to the level of the value for Example 4 (see Figure 6), despite the latter comprising a higher proportion of polyolefin.

C. Creep

The creep behaviour of the polymer blends according to the invention was evaluated experimentally as follows.

Sandwich structures of dimensions 90×50×2 mm were manufactured using galvanised DP 500 grade steel of a thickness of 0.5 mm, which had been degreased (gardoclean® 5183) and chemically surface treated (Granodine® 1455 sold by Henkel, 2% solution in water). The steel-polymer-steel

sandwiches were pressed with the assistance of wedges to maintain a constant polymer thickness of around 0.8 mm.

The conditions prevailing during cataphoresis were then simulated by holding the sandwich vertically with the assistance of a magnet retaining one of the two facings. This sandwich was then placed for 1 hour in an oven at a temperature of 235°C to ensure complete melting of the polymer. The test setup is illustrated schematically in Figure 8.

The resistance of the sandwich to testing was evaluated by visual examination of the sandwich structures after the test. When no slippage of the facings of the sandwich structures was observed, the polymer blend was deemed to exhibit the necessary creep resistance to withstand cataphoresis.

All the evaluated sandwiches withstood the creep test.

D. Adhesion

The adhesion of the polymer blends to steel was evaluated by means of two different tests.

Pull-off test

In this test, the adhesion of the polymer to the metal was evaluated by means of a pull-off test to standard ISO 4624.

The principle involved measuring the maximum force required to pull off a cylindrical steel dolly which had been treated with Granodine® 1455 (sold by Henkel) and adhesively bonded to an ArcelorMittal DP 800 steel substrate of a thickness of 0.5 mm, likewise treated with Granodine® 1455, via a film of the polymer blend of a thickness of 100 µm. Testing was performed on an Instron machine connected to a computer which recorded the force applied as a function of displacement.

Fractures were observed to be mixed, i.e. fracture occurred both at the steel-polymer interface (adhesive fracture) and in the polymer film (cohesive fracture).

The results are illustrated in Figure 9. It will be noted that the force necessary to pull off the dolly was highly satisfactory for the blends according to Examples 1 to 4.

Peel test

In this test, the adhesion of the polymer to the metal was evaluated by means of a peel test to standard NF T 76-112.

This test was carried out by preparing steel-polymer-steel sandwiches in a Lescuyer 200 bar hydraulic press while maintaining the thickness of the polymer at around 0.7 mm with the assistance of wedges. The resultant sandwiches were then cut into strips 20 cm long and 2.5 cm wide.

Before performing peeling, the peel process was initiated to ensure adhesive fracture between the polymer and the metal. Peeling was then carried out by vertical tension over a length of 10 cm using an Instron peel testing machine. In this case too, fracture was mixed.

Very good adhesion was observed for all the investigated compositions.

In conclusion, the reaction at the interfaces of the functional groups of the polyamide and the modified polyolefin in the blends according to the invention results in a specific structure which brings about rheological properties characterised by the appearance of a yield stress.

Such polymer blends exhibit the qualities required for use in the manufacture of metal-polymer composites because they are extrudable and rigid, while exhibiting appropriate deep drawing behaviour and excellent adhesion to metal.

The presence of a yield stress furthermore ensures resistance to cataphoresis even in the molten state since the blend does not yield providing that the stress does not exceed the yield stress. The yield stress value may be optimised in particular not only by selecting the polyamide and the proportion of modified polyolefin in the blend, but also by adding fillers.

SZABADALMI IGÉNYPONTOK

SZTNH-100022587

1. Kétfázisú polimerkeverék, amely tartalmaz:

(a) egy legfeljebb 210°C olvadáspontú poliamidot,

(b) egy karboxil funkciókat hordozó módosított poliolefint,

melynek reológiai tulajdonságaira ömledékállapotban az jellemző, hogy folyáshatára legalább 50 Pa.

2. Az 1. igénypont szerinti keverék, amely 30-70 tömeg% poliamidot tartalmaz.

3. Az 1. vagy 2. igénypont szerinti keverék, amely 30-70 tömeg% módosított poliolefint tartalmaz.

4. Az 1-3. igénypontok bármelyike szerinti keverék, amelyben a módosított poliolefin módosított polietilén.

5. Az 1-4. igénypontok bármelyike szerinti keverék, amelyben a módosított poliolefin maleinsavanhidriddel módosított.

6. Az 1-5. igénypontok bármelyike szerinti keverék, amelyben a módosított poliolefin 0,01-20 tömeg% karboxil-funkciót hordozó vegyülettel van módosítva a módosított poliolefin végtömegére vonatkoztatva.

7. Az 1-6. igénypontok bármelyike szerinti keverék, amelyben a poliamid egy poliamid 11.

8. Az 1-7. igénypontok bármelyike szerinti keverék, amely tartalmaz egy lényegében véve poliamidból álló folytonos fázist és egy lényegében véve poliolefinből álló diszpergált vagy egymásba hatoló („co-continuous") fázist.

9. A 8. igénypont szerinti keverék, amely, amelyben a diszpergált fázis csomók formájában van jelen, melyek közepes átmérője előnyösen 500 nm-nél kisebb.

10. Az 1-9. igénypontok bármelyike szerinti keverék, amely tartalmaz továbbá 5-20 tömeg% töltőanyagot.

11. Eljárás az előző igénypontok bármelyike szerinti polimerkeverék előállítására, amely tartalmazza a következő lépéseket:

(a) veszünk megfelelő mennyiségű poliamidot és megfelelő mennyiségű karboxil-funkciót hordozó módosított poliolefint; és

(b) a poliamidot és a módosított poliolefint a poliamid olvadási esúcsánál magasabb hőmérsékleten keverjük.

12. Eljárás fém-polimer kompozit előállítására, amely tartalmazza a következő lépéseket:

(i) veszünk egy első fémlemezt, adott esetben a polimerkeverék olvadási hőmérsékletére melegítve;

(ii) az első fémlemezre felviszünk egy 1-10. igénypontok bármelyike szerinti polimerkeveréket fém-polimer kompozit kialakítása céljából;

(iii) kívánt esetben a polimerkeverékre felviszünk egy második fémlemezt, adott esetben a polimerkeverék olvadási hőmérsékletére melegítve fém-polimer-fém kompozit kialakítása céljából; és

(iv) a kompozitot melegítjük a fémmel érintkező polimerkeverék megolvadásáig a tapadás teljessé tétele céljából.

13. Szendvicsszerkezet, amely két fémlemez között egy 1-10. igénypontok bármelyike szerinti polimerkeverék filmet tartalmaz.

14. Borítás, amely egy 1-10. igénypontok bármelyike szerinti polimerkeverékkel bevont fémlemezt tartalmaz.

SZTNH-100022588

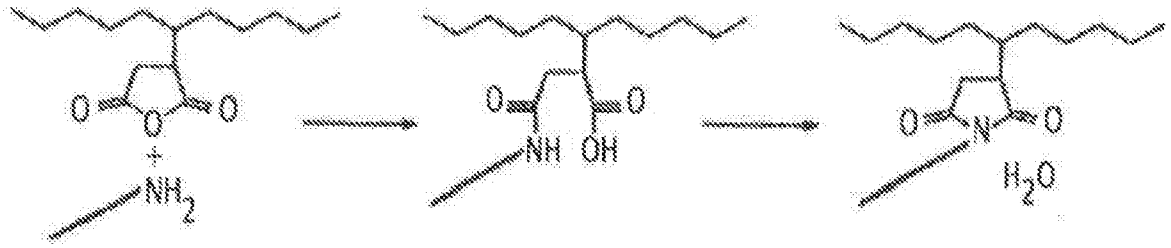


FIG.1

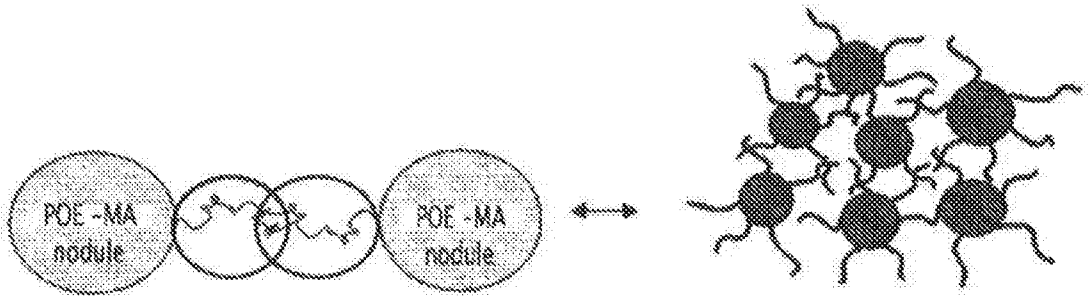
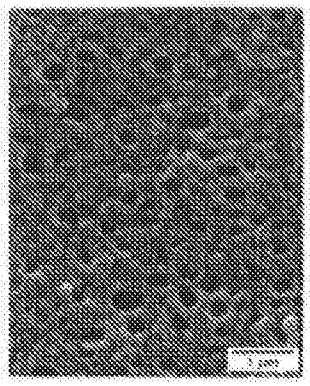
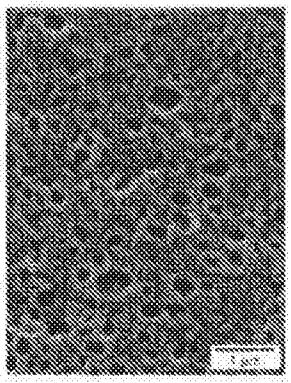


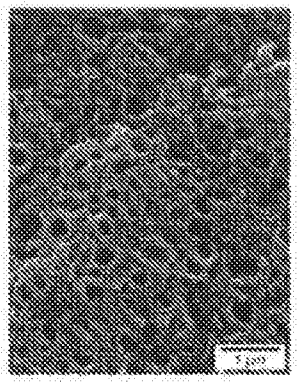
FIG.2



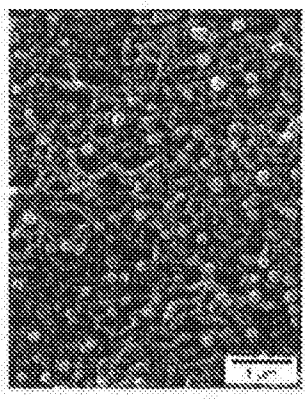
EX. 1



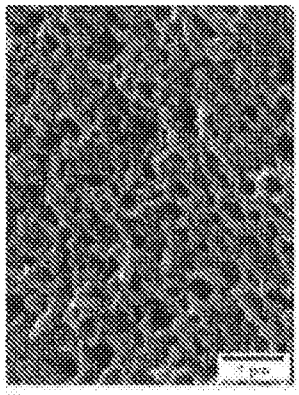
EX. 2



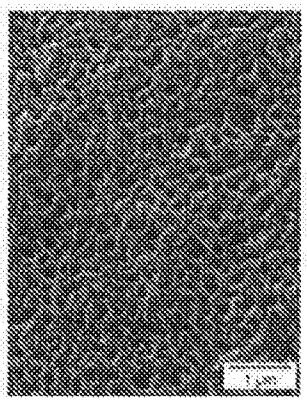
EX. 6



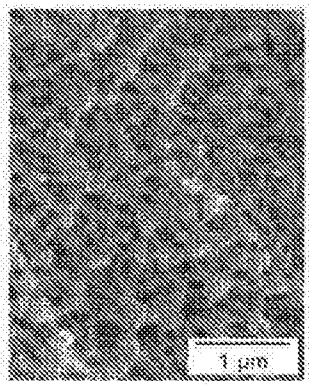
EX. 3



EX. 4



EX. 5



EX. 7

FIG.3

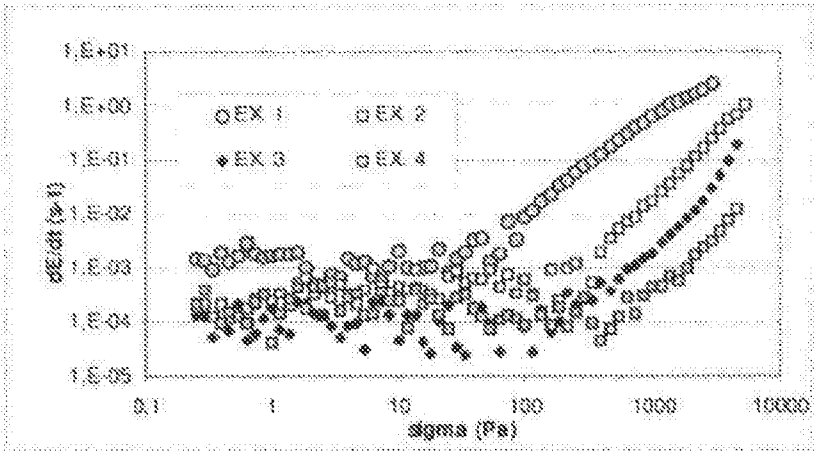

1,E+01
1,E+00
1,E-01
1,E-02
1,E-03
1,E-04
1,E-05
EX. 1
EX. 2
EX. 3
EX. 4
0,1
1
10
100
1000
10000
sigma (Pa)

FIG.4

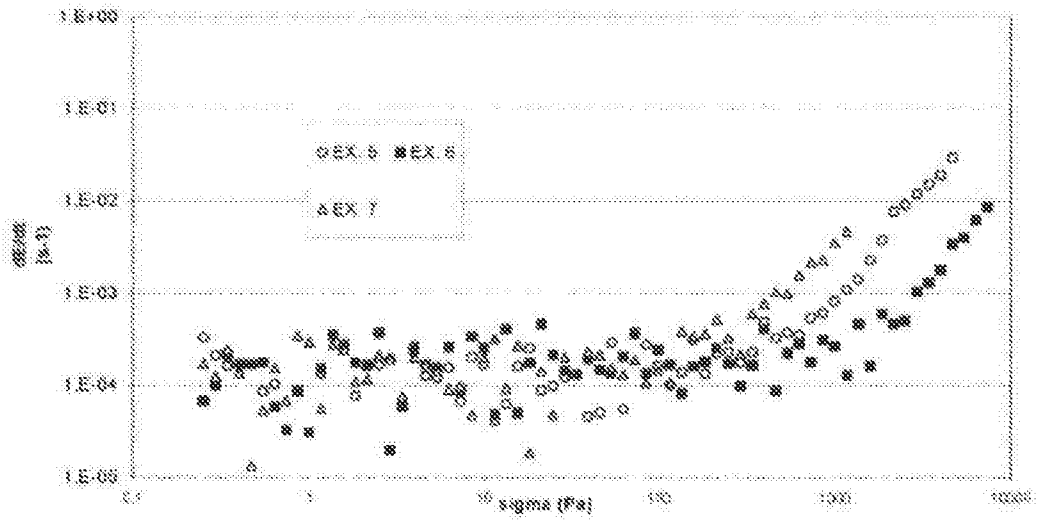

1,E+00
1,E-01
1,E-02
1,E-03
1,E-04
1,E-05
EX. 5
EX. 6
EX. 7
sigma (Pa)

FIG.5

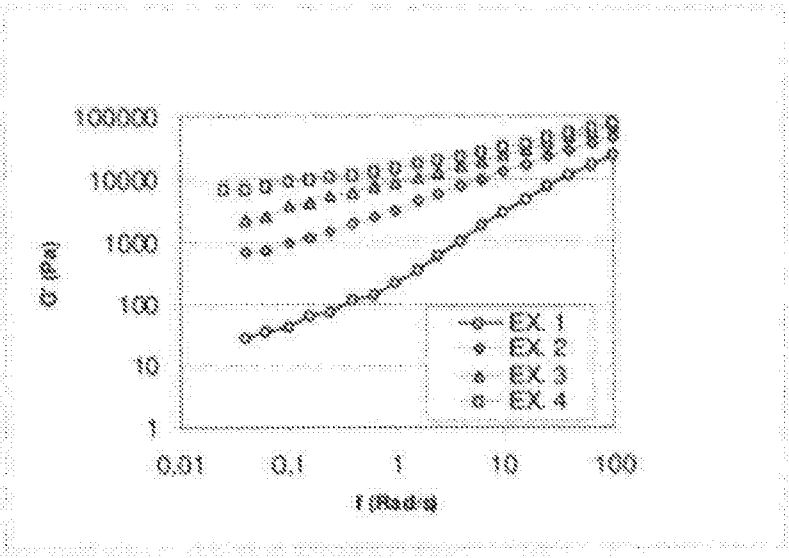

100000
10000
1000
100
10
1
G' (Pa)
0,01
0,1
1
10
100
EX. 1
EX. 2
EX. 3
EX. 4

FIG.6

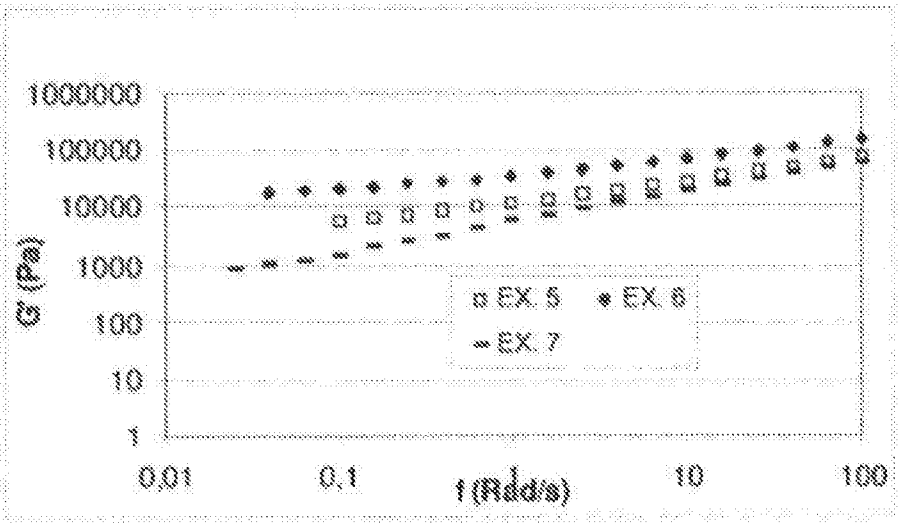

1000000
100000
10000
1000
100
10
1
G' (Pa)
0,01
0,1
1
10
100
f (Rad/s)
EX. 5
EX. 6
EX. 7

FIG.7

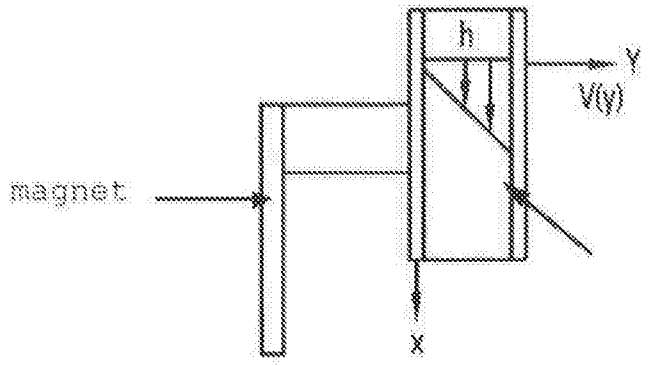

h
Y
V(y)
magnet
x

FIG.8

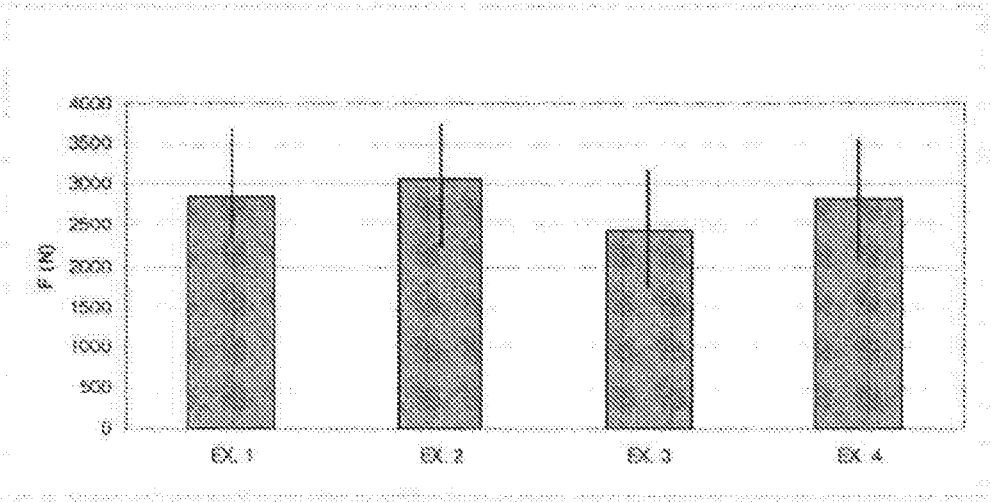

4000
3500
3000
2500
2000
1500
1000
500
0
F (N)
EX. 1
EX. 2
EX. 3
EX. 4

FIG.9