

The present invention relates to a material which is permeable to water vapour and impermeable to water, comprising (i) a film of a thermoplastic elastomer based on polyetheresteramide (ii) associated with a fabric, leather, or a plastic material.

In all that follows, the term film and according to the definition of it given in the Modern Plastics Encyclopedia, refers to a planar section whose thickness is very low in comparison to its length and width.

It is considered that the thickness of a film is generally below 250 μm .

In European Patent published under No. 46 071 there is the description of a water vapour-permeable film consisting of a mixture of polyurethane and of a polymer incompatible with the polyurethane, such as polystyrene.

In European Patent published under No. 141 592 a water vapour-permeable film is proposed, consisting of a mixture of incompatible polymers based on ethylene/vinyl acetate copolymer and on vinyl polymer.

In European Patent published under No. 52 915 there is a description of a polyurethane film which is nonporous and permeable to gases.

Now, the permeability of these films to gases and in particular to water vapour is not very satisfactory, this being especially so in the case of films of low, or even of very low thickness.

The film of the invention exhibits, at equal thickness, a water vapour permeability which is improved in relation to the films mentioned above and its properties remain highly satisfactory in the case of low thicknesses.

The film in accordance with the invention is made of polyetheresteramide-based polymeric material of thermoplastic elastomer type.

Polyetheresteramides are intended to mean both random polyetheresteramides (that is those formed by random chain sequencing of various monomeric constituents) and block polyetheresteramides, that is to say those made up of blocks exhibiting a certain chain length

of the various constituents.

The polyetheresteramides are the product of the copolycondensation of polyamide blocks containing reactive ends with polyether blocks containing reactive ends, such as, among others:

- polyamide blocks containing dicarboxylic chain ends with polyetherdiol blocks.

Such products have been described, for example, in French Patents No. 74 18913 and 77 26678, the content of which must be added to the present description, and in Patent Applications EP 25 288, J 60-063225 and J 63-301223.

The number-average molecular mass of these polyamide blocks is generally between 500 and 10 000 and more particularly between 600 and 5 000. The polyamide blocks of polyetheresteramides are preferably made up of polyamide 6, 6.6, 6.12, 11, 12 or 12.12 (PA-6, PA-6.6, PA-6.12, PA-11, PA-12, PA-12.12) or of copolyamides resulting from the polycondensation of their monomers.

The number-average molecular mass of the polyethers is generally between 200 and 6 000 and more particularly between 600 and 3 000.

The polyether blocks preferably consist of polytetramethylene glycol (PTMG), polypropylene glycol (PPG) or polyethylene glycol (PEG), homo- or copolymerized.

The inherent viscosity of the polyetheresteramides is advantageously between 0.8 and 2.05.

The inherent viscosity is measured in meta-cresol at 20°C with an initial concentration of 0.5 g per 100 g of meta-cresol. It is expressed in dl g^{-1} .

The polyetheresteramides according to the invention may be made up of 5 to 85 % by weight of polyether and of 95 to 15 % by weight of polyamide, and preferably of 20 to 85 % by weight of polyether and 80 to 15 % by weight of polyamide.

Among the polyetheresteramides which are suitable for the invention, the Applicant Company has noted that some were particularly permeable to water vapour: these

are polyether block amides in which the polyether blocks contain homo- or copolymerized PEG and preferably those in which the polyamide blocks are derived from PA-12, PA-11, PA-12.12, homo- or copolymerized, such as for example co-PA-6.12.

The mixture of polymeric material which forms the polyetheresteramide-based film of the invention may optionally contain organic or inorganic fillers.

Silica and titanium oxide may be especially mentioned as examples of fillers.

The mixture may also contain various additives such as anti-UV agents, demoulding agents, impact modifiers, etc., and also colorants or pigments.

Up to 60 % of the total weight of the film of various fillers and/or additives can be added.

The films of the invention which are particularly preferred by the Applicant Company are those whose moisture regain (measured by immersing in water a test specimen 1.6 x 40 x 170 mm in size at 23°C for 24 hours) is less than 120 % of the initial weight of the test specimen before immersion, preferably less than 110 % and advantageously less than 50 %.

The conversion of the mixture described above into film can be carried out according to any known extrusion process, such as extrusion-flat calendering extrusion-coating and blow-extrusion. The said mixture may be treated in the molten state in a single- or twin-screw extruder.

In general, the extrusion temperature is between 190 and 220°C, and preferably between 200 and 210°C.

As described above, the films have a thickness of below 250 μm .

The thickness of the films in accordance with the invention may be advantageously between 8 and 150 μm and preferably between 8 and 100 μm and, better, between 8 and 60 μm .

The polyetheresteramide-based films in accordance with the invention exhibit good mechanical, physical and chemical properties.

Among the properties offered by the films of the invention there may be mentioned, in particular:

- flexibility and impact strength at low temperature,
- good dynamic properties,
- easy processability,
- good acceptability of various fillers and additives,
- and permeability to water vapour and to many gases.

The films of low thickness (below 60 μm) exhibit not only good water vapour permeability properties but also good physical and chemical properties, and especially mechanical properties.

They are particularly preferred within the scope of the present invention, because they permit a significant saving in material in comparison with other films, for example those based on polyurethane which, at equal permeability, are thicker.

All the properties listed above make it possible to employ polyetheresteramide-based films in accordance with the invention in many applications and especially for articles and objects provided with such film(s) and intended for contact with the human or animal body.

The materials of the invention are advantageously employed in the manufacture of clothing and/or footwear, especially those intended for sports and leisure activities.

The films may be bonded to substrates such as fabric, leather, plastic, etc., for example when heated, or with the aid of an appropriate bonding agent. The films thus bonded can be placed either inside the garment or the shoe, or outside.

It is also possible to insert the films of the invention between layers of materials which are identical or otherwise; in this case, the films may remain free or may be bonded, as indicated above, to one or more of the materials.

- The films of the invention are advantageously

suitable for medical usages.

They are particularly suitable for the development of adhesive or nonadhesive dressings, of compresses, etc., and also for the linen employed in operating units.

These films can also be involved in the manufacture of hardware supports for curative or preventive medications administered transcutaneously. In this case, the active substances may be incorporated in the film when it is processed.

- The films according to the invention are advantageously employed for the manufacture of seats and more particularly of motor vehicle seats.

During the manufacture of a motor vehicle seat it is possible, for example, to lay the surface fabric or coating against the mould and then to cover it with a film according to the invention before filling the interior of the mould with foam, which has the effect of properly flattening the said film against the surface fabric or coating.

- The films in accordance with the invention may also be employed advantageously in the building field.

It is possible, for example, to place such films under roofing materials and over the whole surface of the roof in order to permit the removal of moisture from the building and to increase the leakproofing of the roof, without, however, the said moisture being retained by the film.

The following examples illustrate the invention.

EXAMPLE 1

A. Granules of polyetheresteramide are introduced into an extruder.

The whole is heated to a temperature of between 190 and 220°C.

At the die exit, a polyetheresteramide-based film with a thickness equal to approximately 55 μm is obtained.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated polyamide 12 blocks of $\overline{\text{Mn}} = 600$ with α,ω -dihydroxylated

polytetramethylene glycol blocks of $M_n = 2000$.

The polyetheresteramide consists of 23 % by weight of PA-12 blocks and 77 % by weight of PTMG blocks.

The water vapour permeability of the film described above is tested at $22^\circ\text{C} \pm 2^\circ\text{C}$ and at $38^\circ\text{C} \pm 1^\circ\text{C}$ according to the following test, developed by the Applicant Company.

A disc of a diameter below or equal to 10 cm is cut from the film thus obtained and its surface area S is calculated.

The disc is then placed on an adjustable support inside a leakproof enclosure whose moisture content is kept constant (100 % relative humidity) and the temperature θ is kept constant with $\theta \equiv 22^\circ\text{C} \pm 2^\circ\text{C}$ and $\theta \equiv 38^\circ\text{C} \pm 1^\circ\text{C}$.

One face of the disc is left in contact with the moist atmosphere of the enclosure, while the other is swept by a dry nitrogen stream at a constant rate equal to approximately 100 ml/min.

The water vapour diffuses through the thickness e of the disc and is then entrained by the nitrogen stream when it reaches the face of the disc which is swept by the nitrogen stream.

When the quantity of entrained water vapour has stabilized (in general after a few hours), the nitrogen flow is connected to a coulometer in order to measure the quantity of water q entrained during a specified time t (in general between 10 s and 10 min).

5 to 6 measurements are carried out for each test and the mean value of the permeability p , p' to water vapour is calculated for a temperature θ and a degree of humidity, which are given:

$$p = \frac{q \times 24 \times 60}{t \times S} \quad (\text{expressed in g/m}^2 \text{ 24 h})$$

$$p' = \frac{q \times 24 \times 60 \times e}{t \times S} = p \times e \quad (\text{expressed in g mm/m}^2 \text{ 24 h})$$

The results are collated in Table I.

The water vapour permeability of the said film is also measured according to NF standard G 52-019 (expressed in $\text{g/m}^2/24 \text{ h}$), as is the evaporative resistance R_{et} in accordance with DIN standard 54-101 Teil 1 (expressed in $\text{m}^2 \text{ mbar/W} \times 10^3$).

The results are collated in Table II.

B. By way of comparison, the water vapour permeability is measured of a polyester-based polyurethane film with a thickness of approximately $53 \mu\text{m}$ under the same conditions as in A.

The relative density of the polyurethane is equal to 1.19, its Shore A hardness, measured according to ASTM standard D 2240 is equal to 86, and its melting range is between 200 and 230°C .

The results are recorded in Table I.

C. By way of comparison, the water vapour permeability of a polyether-based polyurethane film with a thickness of approximately $51 \mu\text{m}$ is measured under the same conditions as in A.

The relative density of the polyurethane is equal to 1.12, its Shore A hardness, measured according to ASTM standard D 2240 is equal to 85 and its melting range is between 190 and 220°C .

The results are listed in Table I.

D. A film of the same composition as in A, with a thickness equal to approximately $30 \mu\text{m}$ is produced under the same conditions as described in A.

The water vapour permeability and the evaporative

resistance of this film are measured under the same conditions as in A.

The results are collated in Table II.

EXAMPLE 2

A. A polyetheresteramide-based film with a thickness of approximately 75 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide is obtained by copolycondensation of α,ω -dihydroxylated PA-12 blocks of $\overline{M}_n = 2000$ with α,ω -dihydroxylated PTMG blocks of $\overline{M}_n = 2000$.

The polyetheresteramide consists of 50 % by weight of PA-12 and of 50 % by weight of PTMG.

The water vapour permeability of the film described above is tested at $22 \pm 2^\circ\text{C}$ and at $38 \pm 1^\circ\text{C}$ in the same way as in Example 1.

The results are expressed in $\text{g mm/m}^2 24 \text{ h}$ and in $\text{g/m}^2 24 \text{ h}$ and are collated in Table I.

B. A film of the same composition as in A but with a thickness of approximately 107 μm is produced under the same conditions as those described in A. The water vapour permeability of this film is measured under the same conditions as described under A.

The results are collated in Table I.

C. A film of the same composition as in A but with a thickness of approximately 185 μm is produced under the same conditions as described under A. The water vapour permeability of this film is measured under the same conditions as in A.

The results are collated in Table I.

D. A film of the same composition but with a thickness of approximately 12 μm is produced under the same conditions as described under A.

The water vapour permeability and the evaporative resistance of this film are measured under the same conditions as under A.

The results are collated in Table II.

E. A film of the same composition but with a thickness of approximately 18 μm is produced under the same conditions as described under A.

The water vapour permeability and the evaporative resistance of this film are measured under the same conditions as under A.

The results are collated in Table II.

EXAMPLE 3

A polyetheresteramide-based film with a thickness of approximately 30 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{M}_n = 850$ with α,ω -dihydroxylated PTMG blocks of $\overline{M}_n = 2000$.

The polyetheresteramide is composed of 30 % by weight of polyamide blocks and of 70 % by weight of polyether blocks.

The water vapour permeability of the said film and its evaporative resistance are measured in accordance with the standards described in Example 1.A.

The results are collated in Table II.

B. A film of the same composition as in A but whose thickness is approximately 50 μm is produced under the same conditions as in A.

The water vapour permeability of the above film and its evaporative resistance are measured under the same conditions as those described under A.

The results are collated in Table II.

EXAMPLE 4

A polyetheresteramide-based film with a thickness of 12 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{M}_n = 2000$, with α,ω -dihydroxylated PTMG blocks of $\overline{M}_n = 1000$.

The polyetheresteramide is composed of 67 % by weight of polyamide blocks and of 33 % by weight of polyether blocks.

The water vapour permeability of the said film and its evaporative resistance are measured in accordance with the standards described in Example 1.A.

The results are collated in Table II.

B. A film of the same composition as in A but with a thickness equal to approximately 18 μm is produced under the same conditions as described under A.

The water vapour permeability of this film and its evaporative resistance are measured under the same conditions under A.

The results are collated in Table II.

EXAMPLE 5

A polyetheresteramide-based film with a thickness of 12 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{M}_n = 4000$, with α,ω -dihydroxylated PTMG blocks of $\overline{M}_n = 1000$.

The polyetheresteramide is composed of 80 % by weight of polyamide blocks and of 20 % by weight of polyether blocks.

The water vapour permeability of the said film and its evaporative resistance are measured in accordance with the standards described in Example 1.A.

The results are collated in Table II.

B. A film of the same composition as in A but with a thickness equal to approximately 18 μm is produced under the same conditions as described under A.

The water vapour permeability of the above film and its evaporative resistance are measured under the same conditions under A.

The results are collated in Table II.

C. A film of the same composition but with a thickness of approximately 30 μm is produced under the same conditions as described under A.

The water vapour permeability and the evaporative resistance of this film are measured under the same conditions under A.

The results are collated in Table II.

EXAMPLE 6

A polyetheresteramide-based film with a thickness of 12 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{M}_n = 5000$, with α,ω -dihydroxylated PTMG blocks of $\overline{M}_n = 650$. The polyetheresteramide is composed of 88 % by weight of polyamide blocks and of 12 % by weight of polyether blocks.

The water vapour permeability and the evaporative resistance of the film are measured in the same way as in accordance with the standards described in Example 1.A.

The results are collated in Table II.

B. A film of the same condition but with a thickness of approximately 18 μm is produced under the same conditions as described under A.

The water vapour permeability and the evaporative resistance of this film are measured under the same conditions as under A.

The results are collated in Table II.

C. A film of the same composition but with a thickness of approximately 30 μm is produced under the same conditions as described under A.

The water vapour permeability and the evaporative resistance of this film are measured under the same conditions as under A.

The results are collated in Table II.

EXAMPLE 7

A polyetheresteramide-based film with a thickness of approximately 70 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{\text{Mn}} = 650$ with α,ω -dihydroxylated PTMG blocks of $\overline{\text{Mn}} = 1500$.

The polyetheresteramide is composed of 30 % by weight of polyamide blocks and of 70 % by weight of polyether blocks.

The water vapour permeability of the film described above is measured according to the test developed by the Applicant Company such as described in Example 1.A.

The results are collated in Table I.

EXAMPLE 8

A polyetheresteramide-based film with a thickness of approximately 78 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{\text{Mn}} = 1500$ with α,ω -dihydroxylated PEG blocks of $\overline{\text{Mn}} = 1500$.

The polyetheresteramide is composed of 50 % by weight of polyamide blocks and of 50 % by weight of polyether blocks.

The water vapour permeability of the film is measured according to the test developed by the Applicant Company, described in Example 1.A.

The results are collated in Table I.

B. A film of the same composition as in A but whose thickness is approximately 18 μm is produced under the same conditions as in A.

The water vapour permeability and the evaporative resistance of the above film are measured in accordance with the standards described in

Example 1.A.

The results are collated in Table II.

C. A film of the same composition as in A but whose thickness is approximately 50 μm is produced under the same conditions as in A.

Its permeability and its evaporative resistance are measured under the same conditions as in B.

The results are collated in Table II.

D. A film of the same composition as in A but whose thickness is approximately 100 μm is produced under the same conditions as in A.

Its permeability and its evaporative resistance are measured under the same conditions as in B.

The results are collated in Table II.

EXAMPLE 9

A polyetheresteramide-based film with a thickness of approximately 100 μm is produced under the same operating conditions as those described in Example 1.

The polyetheresteramide employed is obtained by copolycondensation of α,ω -dicarboxylated PA-12 blocks of $\overline{Mn} = 4500$, with α,ω -dihydroxylated PEG blocks of $\overline{Mn} = 1500$.

The polyetheresteramide is composed of 75 % by weight of polyamide blocks and of 25 % by weight of polyether blocks.

The water vapour permeability of the film is measured according to the test developed by the Applicant Company and described in Example 1.A.

The results are collated in Table I.

B. A film of the same composition as in A but whose thickness is approximately 18 μm is produced under the same conditions as in A.

The water vapour permeability and the evaporative resistance of the above film are measured according to the standards described in Example 1.A.

The results are collated in Table II.

C. A film of the same composition as in A but whose thickness is approximately 50 μm is produced under the same conditions as in A.

Its permeability and its evaporative resistance are measured under the same conditions as in B.

The results are collated in Table II.

D. By way of comparison, a polyester-based polyurethane film with a thickness of approximately 100 μm is employed, its water vapour permeability being measured under the same conditions as described in A.

The relative density of the polyurethane is 1.19,

its Shore A hardness measured according to ASTM standard D 2240 is 86, and its melting range is between 200 and 230°C.

The results are collated in Table I.

E. By way of comparison, the water vapour permeability of a polyether-based polyurethane film with a thickness of approximately 104 μm is measured under the same conditions as described in A.

The relative density of the polyurethane employed is 1.12, its Shore A hardness, measured according to ASTM standard D 2400, is 85 and its melting range is between 190 and 220°C.

The results are collated in Table I.

EXAMPLE 10

A polyetheresteramide-based film is produced under the same operating conditions as described in Example 1, with a thickness of approximately 18 μm .

The polyetheresteramide employed is obtained by copolycondensation of coPA 6/12 blocks and of PPG/PTMG copolyether blocks.

The coPA 6/12 of $M_n = 1300$ consists of 50 % by weight of PA-6 and of 50 % by weight of PA-12.

The copolyether consists of 80 % by weight of PPG of $M_n = 600$ and of 20 % by weight of PTMG of $M_n = 650$.

The polyetheresteramide is composed of 66 % by weight of copolyamide blocks and of 34 % by weight of copolyether blocks.

The water vapour permeability and the evaporative resistance of the film are measured according to the

standards defined in Example 1.A.

The results are collated in Table II.

B. A film of the same composition as in A but whose thickness is approximately 30 μm is produced under the same conditions as in A.

Its permeability and its evaporative resistance are measured under the same conditions as in A.

The results are collated in Table II.

Measurement of the moisture regain

Test specimens of various polyetheresteramides 1.6 x 40 x 170 mm in size are produced and their moisture regain is tested after 24 hours' immersion in water at 23°C.

The moisture regain of test specimens 50 x 50 x 4 mm in size is also tested after 15 days at 23°C at 50 % relative humidity (RH).

The results are collated in Table III and are expressed as percentages by weight relative to the initial weight of the sample.

TABLE I

EX	FILM THICKNESS (μm)	FILM COMPOSITION	PERMEABILITY TO WATER VAPOUR			
			at $22 \pm 2^\circ\text{C}$		at $38 \pm 1^\circ\text{C}$	
			g mm/m^2 24 h	g/m^2 24 h	g mm/m^2 24 h	g/m^2 24 h
1.A	55	Polyether- esteramide	11.5	209	a	a
1.B (COMPA)	53	Polyester-based polyurethane	8.5	160	20	408
1.C (COMPA)	51	Polyether-based polyurethane	8	157	22	426
2.A	75	Polyether- esteramide	14	187	46	613
2.B	107	Polyether- esteramide	14	131	50	463
2.C	185	Polyether- esteramide	16.5	89	59	322
7	70	Polyether- esteramide	20	286	a	a
8.A	78	Polyether- esteramide	19.2	246	a	a
9.A	100	Polyether- esteramide	11.9	119	51	537
9.D (COMPA)	100	Polyester-based polyurethane	10	100	26	255
9.E (COMPA)	104	Polyether-based polyurethane	9.5	91	25	263

a = too permeable (condensation on the apparatus)

TABLE II

EX No.	THICKNESS (μm)	$R_{et} \times 10^3$ $\text{m}^2 \text{ mbar/W}$	PERMEABILITY TO WATER VAPOUR $\text{g/m}^2/24 \text{ h}$
1.A	55	554	1310 *
1.D	30	240	2510 *
2.D	12	458	1430 *
2.E	18	608	1280 *
3.A	30	453	1890 *
3.B	50	758	940 *
4.A	12	580	1180 *
4.B	18	845	830 *
5.A	12	1061	610 *
5.B	18	1901	310 *
5.C	30	1412	580 *
6.A	12	2803	220 *
6.B	18	2804	270 *
6.C	30	3793	1560 *
8.B	18	65	5350
8.C	50	89	4880
8.D	100	172	4180
9.B	18	113	3630
9.C	50	315	2550
10.A	18	644	1000
10.B	30	796	810

* Much condensation on the surface of the test specimen

TABLE III

Polyetheresteramide type	Moisture regain (%)	
	24 h/water at 23°C	15 days at 23°C 50 % RH
EX 1	1.25	
EX 2	1.12	
EX 3	1.25	
EX 4	0.93	
EX 5	0.51	
EX 6	0.33	
EX 7	109	1.8
EX 8	48	1.4
EX 9	12	0.9
EX 10	3.5	1.3
X	120	4.5

The polyetheresteramide X consists of 50 % by weight of PA-6 blocks of $\bar{M}_n = 1500$ and of 50 % by weight of PEG blocks of $\bar{M}_n = 1500$.

C L A I M S

1. Material which is permeable to water vapour and impermeable to water, comprising
 - (i) a film of a thermoplastic elastomer based on polyetheresteramide
 - (ii) associated with a fabric, with leather, or with a plastic material.
2. Material according to Claim 1, characterized in that the moisture regain of the film after 24 hours' immersion in water at 23°C is less than 120 % of its initial weight.
3. Material according to Claim 2, characterized in that the moisture regain is less than 110 % and preferably less than 50 %.
4. Material according to any one of Claims 1 to 3, characterized in that the film is made of polyether block amide in which the polyether sequences contain homo- or copolymerized polyethylene glycol.
5. Material according to Claim 4, characterized in that the polyamide sequences contain PA-11 and/or PA-12 and/or PA-12,12, homo- or copolymerized.
6. Material according to any one of Claims 1 to 5, characterized in that the film contains up to 60 % by weight of various fillers and additives.
7. Material according to any one of Claims 1 to 6, characterized in that the thickness of the film is less than 250 μm .
8. Material according to Claim 7, characterized in that the thickness of the film is between 8 and 150 μm .



9. Material according to Claim 8, characterized in that the thickness of the film is between 8 and 100 μm , and preferably between 8 and 60 μm .