

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 June 2010 (17.06.2010)

PCT

(10) International Publication Number
WO 2010/066647 A1

- (51) **International Patent Classification:**
C08K 9/04 (2006.01) *H01L 51/52* (2006.01)
C08L 63/00 (2006.01)
- (21) **International Application Number:**
PCT/EP2009/066445
- (22) **International Filing Date:**
4 December 2009 (04.12.2009)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
MI2008A002206 12 December 2008 (12.12.2008) IT
- (71) **Applicant (for all designated States except US):** SAES GETTERS S.p.A. [IT/IT]; Viale Italia 77, I-20020 Lainate MI (IT).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** BONUCCI, Antonio [IT/IT]; Via Chiarelli 8/M, I-20151 Milano MI (IT). MACCHI, Roberto [IT/IT]; Via Varese 28, I-21058 Solbiate Olona VA (IT). GIANNANTONIO, Roberto [IT/IT]; Via Montagnina 9, I-28047 Oleggio NO (IT).
- (74) **Agents:** ADORNO, Silvano et al.; Società Italiana Brevetti S.p.A., Via Carducci 8, I-20123 Milano (IT).

- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) **Title:** COMPOSITE MATERIAL FOR THE PROTECTION OF H₂O SENSITIVE DEVICES BASED ON SURFACE FUNCTIONALIZED NANOZEOLITES DISPERSED IN A POLYMERIC MATRIX

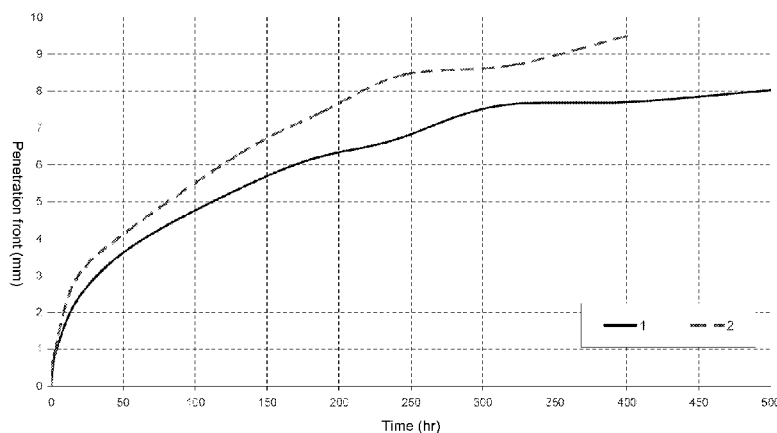


Fig. 1

(57) **Abstract:** The present invention relates to a moisture barrier for the protection of internal environment of sensitive devices comprising a homogeneous dispersion of superficially functionalized containing surface modifying organic group belonging to the same chemical class of at least one functional group of the polymeric compound, to a process for the production of said barrier and to sensitive device comprising such barriers.

WO 2010/066647 A1

**COMPOSITE MATERIAL FOR THE PROTECTION OF H₂O SENSITIVE
DEVICES BASED ON SURFACE FUNCTIONALIZED NANOZEOLITES
DISPERSED IN A POLYMERIC MATRIX**

5 The present invention relates to a composite material for the protection of sensitive devices to the permeation of H₂O from the external environment, the composite material being formed of nanozeolites dispersed in a polymeric matrix.

 It is known that the presence of H₂O, even in the form of traces, is harmful for the correct operation of several devices, among which there are micro-electromechanical
10 devices known in the field as MEMS (Micro-Electro-Mechanical Systems), OLED type organic displays (Organic Light Emitting Diode) and photovoltaic cells such as OSC (Organic Solar Cells) or DSSC (Dye-Sensitized Solar Cells), to mention some of the most interesting ones. In the following, reference will be made to these devices and more generally to any sealed device wherein the presence of H₂O, even in small
15 amounts (lower than 5000 ppm), results to be harmful, with the wording "sensitive device".

 The presence of H₂O in sensitive devices may cause the progressive deterioration of their performances. More information as to the effects of this contaminant may be found in the scientific paper "Correlation between dark spot growth and pinhole size in
20 organic light-emitting diodes", by Shuang Fang Lim, et al., published on Applied Physics Letters, Vol. 78 No. 15, on 9 April 2001 concerning OLED displays, and in the fifth chapter of the book "Organic Photovoltaics - Concepts and Realization" by Brabec et al., published in 2003 by Springer-Verlag, concerning OSC type photovoltaic cells.

 The use of sorbents for the removal of gaseous impurities from the housings of
25 devices sensitive to their presence is known in the art. For example, the international patent publication WO 2004/072604 in the applicant's name discloses the use of active components dispersed in suitable porous matrices; on the other hand international patent publications WO 2007/013118 and WO 2007/013119, both in the applicant's name, disclose nanostructured systems in which the active component is restricted in a porous
30 means that are dispersed in a polymeric matrix, while the use of functionalized nuclei dispersed in a permeable polymeric matrix is disclosed in the international publication

WO 2007/074494, also in the applicant's name.

However, the use of the above-described solutions may be not sufficient to extend the life of the sensitive device up to a length of time compatible with its application field, especially when the permeation flux of H₂O is at a higher speed than the gettering
5 flux specified by the sorbing properties of the composite getter. The permeation speed from the external environment in fact depends on how the device is sealed during the manufacturing step, i.e. on the chemical-physical characteristics of the material used for such a sealing.

During the whole life of the device, the sealing material must be able to act as a
10 barrier in order to protect the packaged device from possible contaminants coming from the outside environment. If the permeation of these contaminants through the sealant is such to lead to the saturation of the getter material inserted in the device after a time that is too short or, anyway, not compatible with the intended application of the device, its protection from possible deterioration processes is not ensured: the barrier shall possess
15 suitable characteristics in term of water permeation in order to guarantee an acceptable lifetime and the presence of the getter material in the sensitive device may have a synergistic effect with the barrier, avoiding its premature saturation. Alternatively, the protection can not be ensured when the effective permeation speed into the device is higher than the sorbing speed of the getter material. Even when the getter material is not
20 inactive due to the saturation if the contaminant is captured with a sorption speed lower than the permeation speed, the damage of the sensitive device element can not be avoided.

In the manufacturing processes of sensitive devices, the use of different polymeric materials to ensure sealing and the protection of the devices from the outer environment,
25 due to their low permeability to the different species of contaminants, is known in the art. For example, the international publication WO 2003/011939 in the name of 3M Innovative Properties Co. discloses that epoxy resins and organic compounds comprising hydroxylic groups can be used as a base for chemical compositions that after a consolidation treatment allow to obtain surface adhesion and low coefficients of
30 moisture transmission rate (commonly referred to as WVTR - Water Vapor Transmission Rate).

Among the suitable additives in these compositions, the use of inert inorganic materials is foreseen in order to reduce the permeation of H₂O in the enclosed environment of the device. However, the use of inert materials limits the barrier properties essentially to those of the final polymeric matrix, and the publication does not
5 tackle the technical problem of achieving a homogeneous dispersion of these inorganic materials associated with the preparation of the composition

Other drawbacks in the case of barriers consisting of a polymeric matrix containing sorbing species featuring a micrometric particle size are given by the difficulties of obtaining sufficiently homogeneous deposits during the manufacturing
10 step of the device especially if thicknesses have to be of about 15 µm or lower. This is coupled with additional difficulties of ensuring a sufficient adhesion to the involved surfaces of the device or of the encapsulant structure after the consolidation process. Moreover, when sealing materials contain sorbing species featuring a nanometric particle size (nanozolites in particular) the limits are more commonly represented by
15 the difficulty of ensuring a homogeneous dispersion of these sorbing species inside the polymeric matrix due to their tendency to agglomerate caused by their high large surface area. The difficulty to control the agglomeration phenomena could cause difficulties to obtain reproducible final properties of the consolidated material and therefore to properly use it in industrial manufacturing processes.

A possible solution for the these composite materials is disclosed in the
20 international publication WO 2008/057045 in the name of Agency For Science Technology And Research, which describes the use of reactive nanoparticles able to sorb water and oxygen molecules inside an epoxy-based composition. However, this document teaches the use of this composition within a multilayer structure able to
25 obtain low permeation values from the outside of the sensitive device. In fact, it is well known in the encapsulation technical field of sensitive devices that better barrier properties are obtained when using one or more sorbing layers (based on a polymeric-getter composite materials or only on getter materials) externally coupled with a so-called (strictly speaking) "sealing layer", i.e. based on a low permeable material but not
30 containing a reactive species. Anyway, these multilayer structure usually need a manufacturing process that is more complex than using a single-layer barrier.

The article "Characterization and preparation of epoxy resin/zeolite nanocomposite" by Chen et al, edited on Diqui Kexue vol. 27, pp.403-407 in 2002 teaches on the use of surfactants or templating agents in order to overcome the difficulties to obtain an homogeneous dispersion of nanoparticles in a polymeric matrix.

5 Similarly, other scientific articles, as for example "Preparation and Characterization of epoxy composites filled with functionalized nano-sized MCM-41 particles" by Wang et al., edited on Journal of Material Sciences, vol. 43, pp. 3683-3688, on 4 April 2008, have studied the effect of inorganic functionalizations or templating agents to improve the interaction between the inorganic particles and the polymeric matrix. All these
10 publications describe different approaches to improve the control on the interaction of the inorganic surface with the organic phase.

As described in the International Patent Application published as WO 2008/000457, the above mentioned nanozeolites can be coated on their surface, where the chemical surface modification is characterized by hydrophobic organic groups
15 bonded by covalent bonds to the zeolite surface. This publication describes some possible applications (related to the uniformity of the nanozeolites in the organic material) for the final composite material that contains them. In particular such reference addresses the problem of the uniformity of the distribution but is completely silent on the effect of the functionalization on the absorption properties of the zeolites
20 and on the quantitative evaluation of its effect on the barrier properties of the sealing material.

It is an object of the present invention to overcome the limits still present in the art concerning the use of sealing materials for devices sensitive to H₂O, by ensuring a homogeneous dispersion of the sorbing species inside a polymeric matrix and, at the
25 same time, by maximizing their barrier properties to avoid as much as possible contaminations from the external environment to packaged elements of a sensitive device. Even if the state of the art shows how the mechanical and/or optical properties of the nanocomposite can be increased, there is no mention of how to improve the barrier properties with reference to beneficial effects given by the introduction of
30 selected ionic species, block-copolymers or surface functionalization, as well as on the preferred chemical compositions of barriers to protect sensitive devices.

In a first aspect thereof the invention is inherent to a barrier composite material against the ingress of H₂O comprising a homogeneous dispersion of superficially functionalized nanozeolites in polymerizable compounds or in a solvent containing them, characterized in that said nanozeolites contain a surface modifying organic group
5 belonging to the same chemical class of at least one functional group of the polymerizable compound. In the description of the present invention a polymerizable compound is defined as an organic composition (that is non or only partially polymerized) where a polymerization process is employed to give a more cross-linked structure by a suitable curing treatment.

10 The invention will be further described by means of Figure 1, showing a comparison of the barrier properties between a composite material according to the present invention and a composite material of the prior art.

In fact, when the use of nanozeolites as reactive species is foreseen, a suitable solution to the above-described problem of achieving a homogeneous dispersion is to
15 functionalize their surface with organic groups in order to reduce their tendency to aggregate and to obtain an unexpected improvement of the barrier properties of the final composite material with respect to a composite material containing non-functionalized or not-suitably functionalized nanozeolites.

Organic functional groups that can be covalently bonded on the surface of the
20 nanozeolites or connected (still by a covalent bond) to the main chain of a polymerizable material can be classified basing on its chemical class: for example, in the following description of the invention, this classification will be considered aliphatic groups such as alkyl-, alkenyl- (e.g. vinyl-) or alkynyl-, aromatic groups as phenyl- or benzyl-. Moreover, functional groups can be classified as amino-, imino-, acrylic- and
25 methacryl-, epoxidic-, isocyanate- etc. groups.

The inventors have found out that, once the polymerizable composition of the preferred sealing resin has been chosen, only some types of functionalization of the nanozeolites can ensure, subsequent to the consolidation step, levels of H₂O penetration that are compatible with the maintenance of inner concentrations of the gaseous species
30 lower than the critical value for time comparable to the desired life of the sensitive device. Thus special chemical formulations have been found, which comprise

precursors of polymeric matrices and also nanometric zeolites superficially functionalized that are to be considered particularly advantageous.

With regard to the characteristic of the polymeric compounds to be used as barrier composite material according to the present invention, the preferred ones exhibit a permeability lower than $10 \text{ g mm m}^{-2} \text{ day}^{-1}$ at 25°C and 60% relative humidity. Concerning the formulation of the dispensable material of the present invention, epoxy resins are particularly suitable as precursors of the polymeric matrix, with particular reference to single component formulations, acrylic (to obtain, for example, polymethylmethacrylate PMMA), urethane (polyurethane PU), olefins (polyethylene PE or HDPE, polypropylene PP, Ethylene propylene rubber EPR) and styrene (polystyrene PS) polymers, as well as isobutylene/isoprene based copolymers (known as butyl rubbers BR). Among epoxy resins, Bisphenol A and epichlorhydrin based resins, known under the acronym DGEBA (Diglycidyl Ether of Bisphenol A), novolak resins and cycloaliphatic resins are particularly advantageous.

Concerning nanometric zeolites that have proved to be suitable to be used as reactive species to be inserted into the polymeric matrix there are surface modified Linde Type A (LTA), Linde Type L (LTL), Faujasite (FAU), Mordenite (MOR) or Gismondine (GIS) zeolites.

With regard to the specific type of their functionalization, the inventors have found that better results can be obtained with particular reference to aromatic groups such as phenyl groups (POD) or pentafluorophenyl groups (PFOD), or organic groups such as vinyl groups (VN), allyl groups (ALL), amino groups (AMP), glycidoxy groups (GTO) methacrylic groups (MCR) or other aliphatic groups (as for example iso-butyl groups OD).

Possible suitable additives present inside the dispensable composition are cationic photoinitiators, plasticizing additives, additives providing flexibility, reactive diluents, consolidating/cross-linking agents and adhesion promoters.

The inventors have found out that barrier properties depend on the composition containing a dispensable material and nanozeolites and mainly can be distinguished in different cases according to different surface functionalization of the nanozeolites:

- a. not organically functionalized;

- b. functionalized by organic groups belonging to different chemical classes with respect to those which are contained in the polymerizable compound;
- c. functionalized by organic groups belonging to the same chemical class but not identical to those which are contained in the polymerizable compound;
- 5 or
- d. functionalized by organic groups belonging to the same chemical class and identical to at least one of those which are contained in the polymerizable compound.

Moreover, in the case d), the identical organic groups present on the surface of the nanozeolites and in the polymerizable compound may be polymerizable groups or not.

The relationship between the particular case among the above reported ones and the barrier properties can be evaluated considering different parameters, as for example the lag time or the breakthrough time. These physical properties are described and studied in the article "Reactive barrier membranes: some theoretical observations regarding the time lag and breakthrough curves" by A. Siegel published on the Journal of Membrane Science, vol. 229 pp. 33–41 in the 2004. These properties can be also related to the effective sorption capacity of the nanozeolites in the polymeric matrix as an effect of the reduced amount of their sorption performance as compared to when they are in the powder form and not incorporated in a matrix.

The inventors have found that the use of functionalized nanozeolites can give better results with respect to both non surface-functionalized nanozeolites and to unloaded polymeric materials. By way of example, Figure 1 shows a formulation that has been found particularly advantageous. This composition provides for the homogeneous dispersion of nanometric zeolites LTA 4A functionalized with aromatic groups POD within a DGEBA based epoxy resin that can be obtained through mechanical stirring. Nanozeolites were previously thermally activated. The obtained composite material has been compared to the case in which not-funzionaliated LTA 4A nanozeolites have been loaded in the same polymeric material.

The permeation front, a parameter which characterized the barrier properties of a given material, has been evaluated using a glass-to-glass configuration where the sealant composition was previously deposited to completely fill the space between the two

5 glasses. This parameter is defined as the length of the barrier material deposit in glass-to-glass configuration corresponding to a specific critical H₂O concentration, that can be different in relation to the final device of interest. Therefore it can be monitored with any analytical techniques able to measure the local amount of H₂O in the polymeric material.

The performance as barrier material for different composite materials can be evaluated by comparing the different times after which the same penetration front has been observed: the relative time, referred to best performing material, have been reported. This parameter, in fact, is evaluated for a chosen H₂O amount but it can be
10 considered as a general property by the assumption that the penetration rate of water is constant in the material (i.e. does not change in function of the water concentration in the polymer).

Table 1 shows some experimental data obtained by comparing the behavior of different composite barriers in terms of the relative time to have the same penetration
15 front. The nanozeolite dispersion in a polymeric matrix (evaluable as the standard deviation in the normal distribution that fits the size spectrum of the agglomerated dispersed phase) does not change meaningfully with their specific functionalization. This is not the case for the barrier properties, that are strongly affected by the specific nature of the functionalization group. Therefore the difference in the barrier
20 performance is not related to the uniformity of the inorganic particle dispersion in the final matrix.

Using, for example, PMMA as polymeric material containing the same weight percent content of active species, not-functionalized nanozeolites (none case) or not-suitably functionalized (POD case) give the same effect on the barrier property of the
25 final material whereas best results have been obtained with crosslinkable identical functional groups in the polymeric material and on the zeolite surface (MCR case). In particular in the reported example it can be observed that PMMA-OD or PMMA-MCR compositions, because of the longer time to have the same penetration front with respect to the PMMA-POD or PMMA-none, can not only protect a sensitive element for longer
30 lasting time (from about 25 to 100%), but also can be used as protective coating or sealing perimetral deposits with reduced dimensions with respect to the comparative

compositions, with obvious advantage in manufacturing and technological development.

In Table 2 other experimental data characterizing the barrier properties of composite materials have been reported, considering different concentration of active species and different kind of adhesive resin, as for example the acrylic resin (for
5 example the Epotek og-603 sold by Epotek Technologies Inc.), a DGBEA-based epoxy glue (Epotek OG-142-17 by Epotek Technologies Inc.) or a cold-setting resin based on two fluid DGBEA-based epoxy components (Epofix by the Struers Inc.).

In a second aspect thereof the invention resides in a method for the use of the compositions of the invention during the encapsulating process of H₂O sensitive
10 devices, in order to protect them from the permeation of this contaminant by means of composite sorbers formed of nanozeolites superficially functionalized with organic groups inside a polymeric matrix.

The inventors have found out that deposition techniques particularly suitable for the compositions of the present invention are serigraphy (screen-printing), micro-
15 dispensing (e.g. using a syringe), spin-coating, spray-coating, doctor blade technique, ink-jet, one-drop process. The deposition process may be so configured to result in a deposit along the edge only of the sensitive device or in an at least partial but preferably complete covering of the element or surface particularly sensible to the presence of moisture in the device.

The consolidation process is carried out after having suitably positioned the two
20 surfaces desired to be coupled. Among the possible processes, UV radiation, thermal consolidation or a combination thereof have proved to be suitable for the present invention. As thermal consolidation, it can be also considered the room temperature curing of a bi-component mixture of precursor organic compounds or the solvent
25 evaporation whenever the precursor is a solution containing the active species and the organic compounds.

In a third aspect the invention consists in a sensitive device wherein the barrier composition of the invention is used for its protection from external contamination, with main reference to moisture and oxygen.

30 Generally, the present invention is advantageous when it is necessary that the concentration of H₂O inside the sensitive device does not exceed a critical value during

the normal operation of the device. This critical value is related to the type of sensitive device, and among the devices requiring a very small water concentration there are the OLEDs, which typically require concentrations of 10 ppm or lower, whereas solar cells may withstand up to 5000 ppm before irreversible deterioration phenomena are generated. Photovoltaic cells (CIS-CIGS cells, CdTe cells, a-Si cells, OSC, DSSC), OLED displays, micro-electromechanical devices (MEMS or MOEMS), Light Emission Diodes (LED) and energy storage devices (with particular reference to lithium batteries and lithium air batteries) are among the sensitive devices that mostly benefit from the application of the method of the invention.

10 The composition of the invention, after its consolidation treatment, can act as the perimetric sealant material of the sensitive device, as perimetral barrier deposit coupled along an outer sealant material of the device or as a barrier layer coating the surface of the structural and/or functional elements of the device that are sensitive to the external environment contaminations. As a limit case, the barrier layer can be used as a filler material that completely fills the encapsulated volume in the sensitive device.

The invention will be further described with reference to the following examples.

Example 1

7.74 grams of LTA 4A-POD previously activated through a thermal process at 240°C under vacuum have been added to 31.36 grams of an Epo-tek OG 142-17 resin (single component commercial epoxy resin based on epichlorhydrin and bisphenol A), viscosity 300-500 cPa s, Tg 54°C. The composition (DGBEAepoxy – POD) has been thus pre-dispersed by means of simple mechanical stirring and subsequently made homogeneous using a so called 3 roll mill mixer. All the operations previously described have been carried out inside a chamber under dry nitrogen atmosphere (generally referred to as "glove box").

A second composition (DGBEAepoxy – none) has been prepared similarly to the procedure above described, using 3.66 grams of non-organically functionalized LTA-4A and 14.50 grams of resin.

Glass-to-glass configurations (one for each composition) have been prepared under a moisture protected atmosphere by depositing 0.22 grams of dispensable material onto a surface of (2.54 x 6.00) cm² in order to achieve a thickness of 300 µm, followed

by UV curing (300 sec, 100mW/cm², λ =250-400 nm).

The kinetic penetration level of H₂O under an exposure condition of each sample at 85°C and with 85% relative humidity is set forth in the graph of figure 1 in the form of a solid line 1 for the composition containing the surface modified zeolites and in the form of the broken line 2 for the non-functionalized case. In table 2 have been reported the relative times to have the same penetration front in the compared samples.

Example 2

230.8 grams of PMMA (Aldrich, MW 120000) were previously dissolved in 800 ml of Toluene anhydrous 99% (Aldrich). A clear viscous PMMA/Toluene suspension has been obtained under reflux heating at 80°C for 30 minutes and mechanical stirring.

The composition PMMA-none prepared adding 1.90 grams of LTA 4A (previously activated 450°C under vacuum) to 30.05 grams of PMMA/Toluene solution has been thus pre-dispersed by means of simple mechanical stirring and subsequently made homogeneous using a so-called 3 roll mill mixer. All the operations were carried out in glove box.

The glass to glass configurations were performed in glove box depositing the composite over a glass substrate 2.54 x 6.00 x 0.015 cm, and gently heated to 50°C for 10 minutes to consolidate the film, then a cover glass was applied and the glass to glass sample were dried under vacuum at 80°C for 6 hours until constant weight of the system was achieved.

Similarly, surface modified nanozeolite containing compositions have been prepared using respectively:

- a) PMMA-POD composition: 1.91 grams of LTA-4A POD (previously activated through a thermal process at 240°C) in 31.32 grams of PMMA/Toluene solution;
- b) PMMA-OD composition: 1.90 grams of LTA-4A OD previously activated through a thermal process at 170°C in 31.50 grams of PMMA/Toluene solution;
- or
- c) PMMA-MCR composition: 1.79 grams of LTA-4A MCR previously activated through a thermal process at 180°C in 29.9 grams of PMMA/Toluene solution.

Glass-to-glass configurations using these compositions have been obtained following the same procedure described for the PMMA-none composition.

In table 2 the relative times to have the same penetration front (testing conditions 85°C and 85% relative humidity) in the compared samples have been reported.

Example 3

1.50 grams of LTA 4A-POD previously activated through a thermal process at 240°C under vacuum have been added to 28.00 grams of an Epo-tek OG-603 resin (single component acrylic resin), viscosity 300-500 cPa s, Tg 54°C. The composition acrylic-POD has been thus pre-dispersed by means of simple mechanical stirring and subsequently made homogeneous using a so-called 3 roll mill mixer. All the operations previously described have been carried out inside a glove-box.

A second composition (acrylic-MCR) has been prepared similarly to the procedure as above described, using 1.05 grams of LTA-4A MCR and 20.03 grams of resin.

Glass-to-glass configurations (one for each composition) have been prepared under a moisture protected atmosphere by depositing 0.49 grams of dispensable material onto a surface of (2.54 x 6.00) cm² followed by UV curing (10 sec, 100mW/cm², $\lambda=250-400$ nm).

The kinetic penetration levels of H₂O under an exposure condition of the sample at 85°C and with 85% relative humidity have been evaluated and in table 2 have been reported the relative times to have the same penetration front in the compared samples.

Example 4

0.42 grams of LTA 4A activated through a thermal process at 450°C under vacuum have been added to a mix of 1.60 grams of Epofix base, 0.07 grams of Epofix hardener (commercial available bicomponent DGEBA epoxy resin) and 0.1 grams of (3-glycidoxypropyl)trimethoxysilane (ABCR). The composition (cold setting epoxy – none) has been thus pre-dispersed by means of simple mechanical stirring and subsequently made homogeneous using a so-called 3 roll mill mixer. All the operations were carried out in glove box.

Similarly, a second composition (cold setting resin – GTO) has been obtained by adding 0.42 grams of GTO (pre-activated through a thermal process at 175°C under vacuum) to a mix of 1.60 grams of Epofix base, 0.07 grams of Epofix hardener and 0.1g of ABCR.

Finally a third composition (cold setting resin – POD) has been obtained, with the same procedure, adding, 0.42 grams of (POD pre-activated through a thermal process at 240°C under vacuum) to a mix of 1.60 grams of Epofix base, 0.07 grams of Epofix hardener and 0.1 grams of ABCR.

- 5 In order to achieve the glass to glass configuration for each composition, they were performed in glove depositing the glue over a glass substrate 2.54 x 6.00 x 0.015 cm and covered with another glass slide. The resins were cured at 80°C for 1 hour.

- The kinetic penetration levels of H₂O under an exposure condition of the sample at 85°C and with 85% relative humidity have been evaluated and in table 2 have been
10 reported the relative times to have the same penetration front in the compared samples.

Table 1

Polymer	Nanozeolite functionalization	w/w%	Relative Time to have the same penetration front	Nanozeolite dispersion
PMMA	none	20%	0,55	12%
PMMA	POD	20%	0,57	13%
PMMA	OD	20%	0,70	10%
PMMA	MCR	20%	1,00	10%

Table 2

Resin	Nanozeolite functionalization	w/w%	Relative Time to have the same penetration front
acrylic	POD	5%	0,75
acrylic	MCR	5%	1,00
DGEBA - epoxy	none	20%	0,81
DGEBA - epoxy	POD	20%	1,00
cold-setting epoxy	none	20%	0,68
cold-setting epoxy	POD	20%	0,95
cold-setting epoxy	GTO	20%	1,00

CLAIMS

1. Barrier composite material against the ingress of H₂O comprising a homogeneous dispersion of superficially functionalized nanozeolites in a polymerizable compound, characterized in that said nanozeolites contain surface modifying organic groups belonging to the same chemical class of at least one functional group of the polymeric compound.
2. Barrier composite material according to claim 1 wherein the surface modifying organic group of the nanozeolites is the same of at least one functional group of the polymerizable compound.
3. Barrier composite material according to claim 1 or 2, wherein said functionalization on the superficially modified nanozeolites comprises aromatic groups.
4. Barrier composite material according to claim 3, wherein said aromatic groups are phenyl groups.
5. Barrier composite material according to claim 1 or 2, wherein at least one of the surface modifying organic group is an aliphatic group.
6. Barrier composite material according to claim 2, wherein the surface modifying group of the nanozeolites is a polymerizable group.
7. Barrier composite material according to claim 6, wherein the surface modifying group is a glycidoxy, acrylic or a methacrylic group.
8. Barrier composite material according to claim 1, wherein said polymerizable compound is an organic resin is an epoxy or acrylic resin.
9. Barrier composite material according to claim 1, wherein said polymeric compound is a novolak resin.
10. Barrier composite material according to claim 1, wherein said surface modified nanozeolites are characterized by the fact of being LTA, FAU, LTL or GIS zeolites.
11. Barrier composite material according to claim 8, wherein the epoxy resin is characterized by the fact of being a single component resin.
12. Barrier composite material according to claim 11, wherein said single component resin is a bisphenol and epichlorhydrin (DGEBA) based resin.

13. Process for making a barrier according to claim 1 by means of a deposition process of a barrier precursor followed by a consolidation process.

14. Process according to claim 13 wherein said deposition is made by means of serigraphy.

5 15. Process according to claim 13 wherein said deposition is obtained by means of microdispersion.

16. Process according to claim 15 wherein said microdispersion is obtained with a syringe.

10 17. Process according to claim 13 wherein said consolidation process is chosen from UV irradiation, thermal and their combination.

18. Sensitive device comprising a barrier composite material according to claim 1.

19. Sensitive device according to claim 18 wherein said barrier composite material is present on the edge of the sensitive device.

15 20. Sensitive device according to claim 18 wherein said barrier composite material covers an inner part of the sensitive device.

21. Sensitive device according to clam 18 wherein said device is a photovoltaic cell.

20 22. Sensitive device according to clam 18 wherein said device is an OLED screen.

23. Sensitive device according to clam 18 wherein said device is a micro-electromechanical devices.

24. Sensitive device according to clam 18 wherein said device is an energy storage device.

25 25. Sensitive device according to clam 24 wherein said device is a lithium battery.

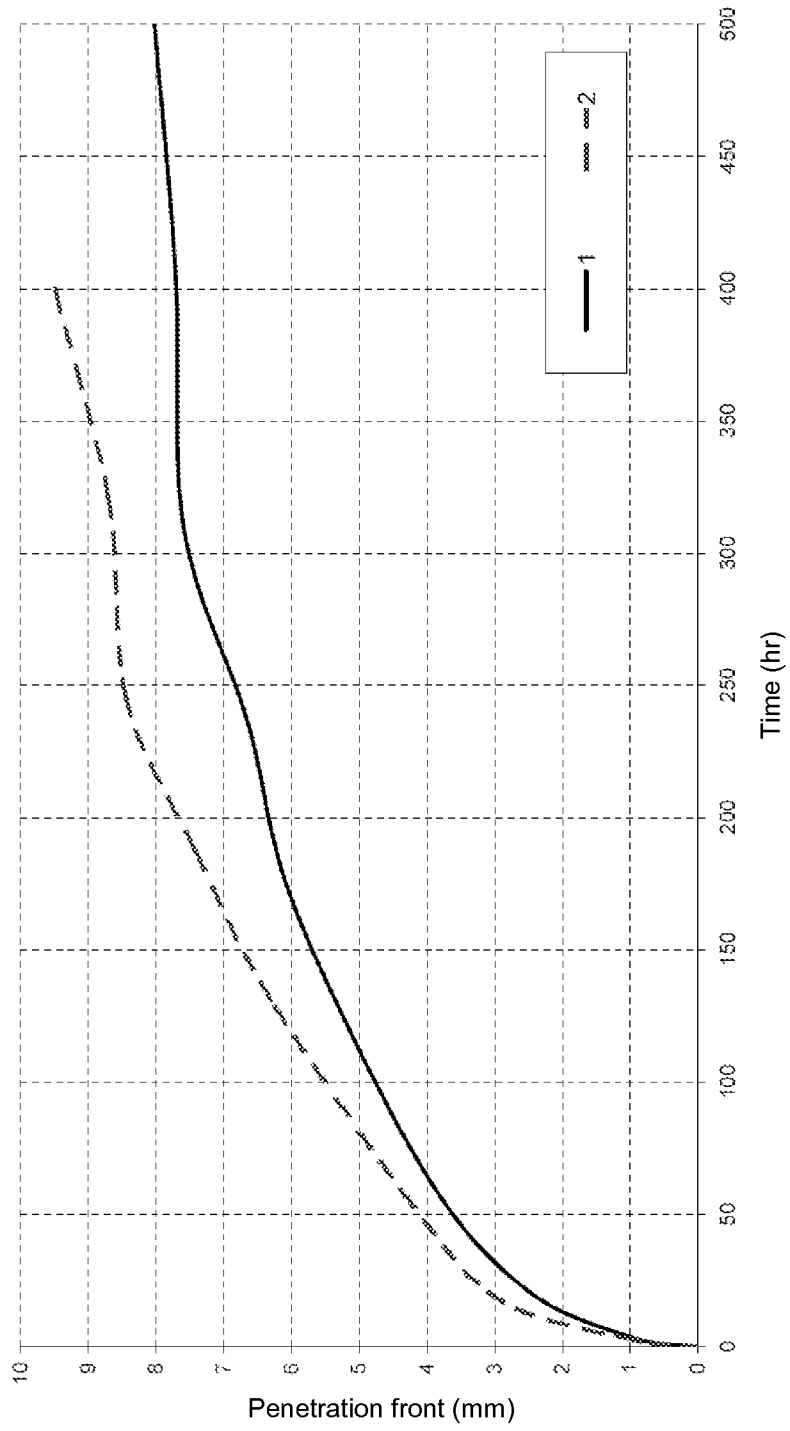


Fig.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/066445

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08K9/04 C08L63/00 H01L51/52

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

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08K H01L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NA WANG, E.A.: "Preparation and characterization of epoxy composites filled with functionalized nano-sized MCM-41 particles" JOURNAL OF MATERIALS SCIENCE, vol. 43, 4 April 2008 (2008-04-04), pages 3683-3688, XP002531814 the whole document ----- -/--	1-6

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 18 March 2010	Date of mailing of the international search report 22/04/2010
---	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer O'Sullivan, Timothy
--	--

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/066445

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CHEMABS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 2002, CHEN, YAN-LING, E.A.: "Characterization and preparation of epoxy resin/zeolite nanocomposite" XP002531815 retrieved from STN Database accession no. 137:356800 abstract & DIQIU KEXUE, vol. 27, no. 4, 2002, pages 403-407, -----</p>	1-6
X	<p>EP 1 873 202 A1 (CLARIANT INT LTD [CH]; UNIV BERN [CH]; OPTICAL ADDITIVES GMBH [CH] CLA) 2 January 2008 (2008-01-02) page 2, line 22 - line 26; claims -----</p>	1-6
A	<p>WO 2007/114822 A1 (NAT STARCH CHEM INVEST [US]; KONG SHENGOIAN [US]; GRIESHABER SARAH E [] 11 October 2007 (2007-10-11) [0037] claims -----</p>	1
A	<p>US 3 704 806 A (PLACHENOV TIKHON GRIGORIEVICH ET AL) 5 December 1972 (1972-12-05) claims; examples 1,2 -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/066445

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 1873202	A1	02-01-2008	CN 101100535 A	09-01-2008
			JP 2008013749 A	24-01-2008
			KR 20080002645 A	04-01-2008
			US 2008014451 A1	17-01-2008

WO 2007114822	A1	11-10-2007	CN 101405321 A	08-04-2009
			EP 2001924 A1	17-12-2008
			JP 2009532519 T	10-09-2009

US 3704806	A	05-12-1972	NONE	
