(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 August 2012 (02.08.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/100315 A1

(51) International Patent Classification:
C08L 1/02 (2006.01) ***C08K 5/5419*** (2006.01)
C08K 3/22 (2006.01)

(21) International Application Number:
PCT/BR2012/000024

(22) International Filing Date:
30 January 2012 (30.01.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
018110002945 28 January 2011 (28.01.2011) BR

(71) Applicants *(for all designated States except US)*: **UNIVERSIDADE ESTADUAL PAULISTA "JÚLIO DE MESQUITA FILHO"** [BR/BR]; Rua Quirino de Andrade,215, Centro, CEP-01049-010 São Paulo, SP (BR). **FUNDAÇÃO DE AMPARO A PESQUISA DO ESTADO DE SÃO PAULO - FAPESP** [BR/BR]; Rua Pio XI, 1500, Alto da Lapa, São Paulo, CEP-05468-901 São Paulo, SP (BR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CAIUT, José Maurício Almeida** [BR/BR]; Rua Pedro Alvares Cabral, 2296, ap. 13, Centro, CEP-14801-390, Araraquara, SP (BR). **BARUD, Hernane da Silva** [BR/BR]; Rua Primo Torquato, 405/02, Jd. Tinem, CEP-14806-108 Araraquara, SP (BR). **MESSADDEQ, Younes** [BR/BR]; Av. Dr. Agostinho Tucci, 1122, Villa Harmonia, CEP-14802-590, Araraquara, SP (BR). **RIBEIRO, Sidney José Lima** [BR/BR]; Rua Dr. Clemente Ferreira, 1135, Jardim Marivam, CEP-14800-000 Araraquara, SP (BR).

(74) Agent: LOPES, Flávia Salim; Clarke, Modet Propriedade Intelectual Ltda., Av. Marechal Câmara, 160, 12° andar, Ed. Le Bourget, CEP-20020-080, Centro, Rio de Janeiro, RJ (BR).

(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, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, 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, RS, 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))*

(54) Title: OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND / OR A BOEHMITE- SILOXANE SYSTEM

(57) Abstract: The present invention comprises composites with multifunctional characteristics, being capable of substituting glass, with significant advantages, with particular emphasis on flexibility, for a variety of applications such as, for example, display screens and others. Among other aspects, the product that constitutes the object of the invention is particularly characterized by rendering bacterial cellulose transparent, in addition to being flexible, biocompatible and able to replace glass in 100% of possible applications. Among other aspects, the development of the composites according to the present invention allows an effective increase in optical transmission, enabling an optical transmission of more than 90%, such transparency being necessary, equally, for the development of medical devices, for example.

WO 2012/100315 A1

OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND / OR A BOEHMITE-SILOXANE SYSTEM

FIELD OF THE INVENTION

This invention is related to the technical field of Chemistry, more specifically to methods for obtaining transparent organic-inorganic composite materials and multifunctional composites that are transparent and flexible.

BACKGROUND OF THE INVENTION

Glass is used frequently in several state-of-the-art applications, such as monitors, screens, television sets, displays and others, due particularly to its transparency, which may vary according to the industrial fabrication processes used. Nevertheless, it is generally known that glass lacks certain specific characteristics, such as flexibility, for example.

The possibility of obtaining devices for optical and electronic purposes, such as electronic paper and OLEDs, by making use of bacterial cellulose has already been known for some years already, although improvements are required, principally in optical transmission, as bacterial cellulose has only 40% transparency (in the visible range of the spectrum).

Thus, it would be desirable to obtain a material that could substitute glass in 100% of its applications, but with the characteristics of flexibility, transparency, high durability and biocompatibility, being fabricated from renewable sources.

An important component has already been detected in this field, which is bacterial cellulose, despite the natural difficulty of making bacterial cellulose transparent.

Initially, the substrates most widely used for preparing electronic devices were made of glass, which is a transparent material with good mechanical resistance. However, one of the limitations of using glass is related to the difficulties in preparing flexible / foldable devices, as glass shatters easily.

Over the past few years, much stress has been laid on the use of polymer-based materials (plastics) as possible substitutes for glass. As an alternative, the use of polymers as substrates for optical and electronic devices could pave the way for obtaining lighter, more flexible and portable systems, with no loss of the necessary transparency and strength. Several polymers – including polyethylene terephthalate (PET), cellulose acetate (CA), polyurethane (PU) and polycarbonate (PC) – have been used to produce flexible devices.

Most of the polymers used today are synthetic or derived from oil, required several additional treatments in order to reach an ideal substrate; in most cases, they are not biocompatible or biodegradable.

Thus, due to its excellent properties and an appearance similar to paper, summarized as transparency, high reflectivity (similar to ordinary paper), flexibility, contrast and biodegradability, bacterial cellulose appears as an interesting matrix for preparing flexible devices.

With regard to its molecular formula, bacterial cellulose is identical to plant-based cellulose (PC), although with a mesh formed by nanometric fibers (nanocellulose); it has a higher proportion of micro-crystalline structures (with up to four different phases), which endows it with characteristics differing from those of plant-based cellulose, high mechanical resistance, better crystallinity than that of plant-based cellulose, permeability to liquids and gases and electric current conduction.

The boehmite-siloxane hybrid is one of the composites at the molecular scale that presents macroscopic properties resulting from the synergy between two component nanometric phases; for example, the variation in the proportions of the phases allows control of the refraction index, in addition to transparency and homogeneity. These materials may be used as transparent coatings with high resistance to abrasion, obtained through curing at low temperatures. However, the mechanical resistance and flexibility of these hybrids are limited. On the other hand, the use of bacterial cellulose in the preparation of the composite, based on the hybrid, endows the boehmite-siloxane system with mechanical resistance and flexibility, in addition to the possibility of producing extremely thin (measured in microns) up to thick (measured in millimeters) composite sheets.

At the current state of the art, some papers and documents are known that justify the need for materials with the characteristics and qualities inferred in this invention.

Particularly noteworthy is US 2005/0079386, which addressed compositions, methods and systems for making and using electronic paper, suggesting the fabrication of OLEDs on flexible cellulose-based substrates applied to the fabrication of paper or electronic displays similar to paper. In this case, the OLEDs would be applied to polymer-based conducting circuits and then to sheets of paper made from bacterial cellulose (produced by the *Acetobacter xylinum* bacteria, for example). These devices open up possibilities for several applications, such as electronic books ("e-books"), electronic newspapers ("e-newspapers"), dynamic wallpapers and others.

Thus, due to its specific properties, such as transparency, with a three-dimensional structure formed by nanofibers and excellent mechanical properties, in addition to being biocompatible, bacterial cellulose appears as a promising material for the preparation of OLEDs.

Within this conception, and still referring to the state of the art, particularly in documents JP2008127510-A, WO2007049666-A1, JP2007146143-A and CN101297000-A, composites are being developed on the basis of bacterial cellulose and epoxy resins, acrylic resins and urethane resins that are used to enhance the transparency of bacterial cellulose. In these cases, transparency is obtained at between 60% and 80%, which is less than that achieved by the proposed invention.

Documents WO2008117848-A1 and JP2008242154-A present the use of composites made from resins (epoxy, acrylic and urethane) for preparing organic light-emitting diodes (OLEDs).

Document CN101274107-A describes the use of a bacterial cellulose composite – a transparent polymer – based on poly-beta-hydroxyethyl methacrylic acid, as a bone support, blood vessel prosthesis and artificial skin.

SUMMARY OF THE INVENTION

Over the past few years, much stress has been laid on the use of polymer-based materials (plastics) as possible substitutes for glass. As an alternative, the use of polymers as substrates for optical and electronic devices could pave the way for obtaining lighter, more flexible and portable systems, with no loss of the necessary transparency and strength.

This invention is related to methods for obtaining composites with multifunctional characteristics that could replace glass (with advantages, mainly flexibility), in assorted applications such as screens, displays and others, for example. Among other aspects, the product addressed by this invention is noteworthy for making bacterial cellulose transparent and flexible, being biocompatible and replacing glass in 100% of the applications.

On purpose of this invention is an optically transparent composite based on bacterial cellulose and boehmite, siloxane and / or a boehmite-siloxane system containing a bacterial cellulose membrane and a hybrid inorganic boehmite compound: 3-glycid oxypropyl trimethoxy silane.

In a preferred materialization of this invention, dry bacterial cellulose membranes or hydrated bacterial cellulose membranes are used, resulting in a composite with transparency between 70% and 100%.

In the same materialization mentioned above, the inorganic hybrid presents an Al:Si proportion between 0.01 Al: 1Si and 100 Al: 1Si, preferably 1Al: 1Si. In this materialization, the bacterial cellulose membranes must present a thickness of between 0.1 and 15 mm, for the dry bacterial cellulose membrane and 1 and 1500 μm for the hydrated bacterial cellulose membrane.

In another materialization of this invention, the inorganic hybrid solution presents concentrations between 2 and 5M, coating at least one of the surfaces of the bacterial cellulose membrane or is incorporated into its pores.

Another purpose of this invention is the process for obtaining optically transparent composites based on bacterial cellulose and boehmite, siloxane and / or a boehmite-siloxane system, characterized by containing at least one of the following steps: production of bacterial cellulose membrane (BC), drying the bacterial cellulose membrane (BC), preparing the Boehmite solution (Boeh), preparing the 3-glycid oxypropyl trimethoxy silane (GTPS) solution, preparing the Boeh-GTPS hybrid, curing the Boeh-GTPS hybrid, immersing the BC in the

Boeh-GTPS solution and drying the BC/Boeh-GTPS composite.

In a preferred materialization of this invention, this process is comprised by the fact that the bacterial cellulose membrane is dried for one to 24 hours in an airflow kiln at a temperature of 40°C.

In the above-mentioned materialization, the Boeh-GTPS hybrid is cured in a kiln at a temperature of 50 °C, with a necessarily reduction of 40% in the indicial volume of the hybrid.

In another materialization of this invention, the bacterial cellulose membrane is immersed in the Boeh-GTPS hybrid solution for 24 hours, after which 24 hours this composite must necessarily be dried for 12 hours in a kiln at a temperature of 40°C.

DESCRIPTION OF THE FIGURES

FIGURE 1 presents images obtained through scanning electron microscopy of the bacterial cellulose – hybrid composite, as follows: sandwich structure (left and center), with the cellulose in the middle of the composite; composite with a bacterial cellulose surface free for subsequent interactions (right);

FIGURE 2 is a graph showing the Optical Transmission Spectrums of: (a) pure bacterial cellulose; (b) BCH/Boe-GPTS composite; (c) BCS/Boe-GPTS composite and (d) Boe-GPTS System.

FIGURE 3 presents images obtained through scanning electron microscopy where: A - bacterial cellulose surface; B - hybrid bacterial cellulose / boehmite-GPTS composite surface; C - fracture of the dry bacterial cellulose composite / boehmite – GPTS coating both sides of the bacterial cellulose; D - fracture of the dry bacterial cellulose composite / boehmite-GTPS coating only one side of the dry bacterial cellulose; E - fracture of the dry bacterial cellulose composite / boehmite-GPTS coated on both sides; F - fracture of the hydrated bacterial cellulose composite / boehmite-GTPS; BC – bacterial cellulose; Boeh-GTPS – boehmite-GTPS composite.

FIGURE 4 presents X-ray diffractograms of: a) bacterial cellulose; *b)* boehmite-GTPS system; c) dry bacterial cellulose composite / boehmite-GPTS; d) hybrid bacterial cellulose composite / boehmite-GPTS; ** boehmite peaks.

FIGURE 5 is a graph showing the TG (___) and DTG (------) curves of: a) bacterial cellulose; b) boehmite-GTPS system; c) dry bacterial cellulose composite / boehmite-GTPS; d) hydrated bacterial cellulose composite / boehmite-GTPS.

FIGURE 6 presents the DSC curves for: a) bacterial cellulose; b) boehmite-GTPS system; c) dry bacterial cellulose composite / boehmite-GTPS; d) hybrid bacterial cellulose composite / boehmite-GTPS.

FIGURE 7 presents a typical Stress x Deformation curve for: a) bacterial cellulose; b) dry bacterial cellulose composite / boehmite-GTPS; c) hybrid bacterial cellulose composite / boehmite-GTPS.

DETAILED DESCRIPTION OF THE INVENTION

The **"OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND / OR A BOEHMITE-SILOXANE SYSTEM"** that are addressed by this invention, describe how to obtain multifunctional composites based on bacterial cellulose and boehmite, siloxanes and / or hybrid boehmite-siloxane systems endowed with applications in the optical and electronic fields (flexible screens, electronic paper, electronic book, solar-powered mobile telephones) and devices in the medical area (contact lenses, ophthalmological dressings, topical dressings and tissue engineering supports), particularly for applications requiring a high level of transparency, among other characteristics, at around 90% for example, as noted in the tests conducted.

In technical terms, multifunctional materials based on bacterial cellulose boehmite, bacterial cellulose-boehmite-siloxane, for possible applications in the optical and electronic fields and / or as medical devices, were developed due to rising demands for flexible and transparent substrates, preferably biocompatible and biodegradable, that could become potential candidates for replacing glass in the fabrication of optical devices.

Thus, the possibility of obtaining optical and electronic devices using bacterial cellulose is already known at the state of the art, although improvements are required, principally for optical transmission, as bacterial cellulose presents transparency of only 40% (in the UV-Vis range), as reported above. The development of new composites would allow an effective increase in optical transmission, with transparency exceeding 90%, through this invention.

To do so, the invention uses highly hydrated bacterial cellulose membranes with different thicknesses of between 0.1 mm and 15 mm, or dry bacterial cellulose membranes with thicknesses of between 1 μm and 1500 μm, which are immersed boehmite, siloxane or boehmite-siloxane solutions at different concentrations of between 0.001 M and 10 M.

Due to the desired application, the bacterial cellulose membranes are coated on both sides, or simply with a single layer, thus conserving the bacterial cellulose layer, particularly for medical applications.

The material obtained in this manner is then dried at 40°C for approximately 24 hours, preferably in frame-type molds.

The experimental procedures used to prepare optically transparent multifunctional composites based on bacterial cellulose and boehmite, siloxane and / or a boehmite-siloxane system are exemplified below, but are not limited to these materializations.

Example 1: Preparation of aluminum oxide hydroxide (Boehmite).

Through this synthetic route, 25 g (0.10 mol) of aluminum tri-sec-butoxide (Organic Acros) were added to 200 mL of water at 83°C, and agitated vigorously. After one hour of agitation 0.440 ml of HNO_3 (Synth, 65%) were added at a rate of 0.07 mol of HNO_3 to 1.0 mol of Al^{3+}. At this 0.07 rate, the gel would acquire less volume and the resulting sol is extremely stable in water. The temperature was raised to 87°C, resulting in the evaporation of the reaction by-products (butanol in this case) after two hours.

Example 2: Preparation of the Boehmite – GPTS hybrid (3-glycid oxypropyl trimethoxy silane).

Through this synthetic route, one liter of boehmite sol (concentration of 0.5M, prepared as described in item 1) was maintained under strong magnetic agitation, adding 110 mL of GPTS. The medium was maintained under agitation for three hours and was then stored in a sealed flask for subsequent use.

This description refers to a proportion of 1:1 aluminum – silicon (mol:mol proportion). Different proportions may be prepared, ranging from 0.01Al: 1Si up to 100Al: 1Si, solely by the variation in the proportion of the Boehmite and GPTS reagents.

Example 3: Curing (aging) process of the Boehmite – GPTS hybrid

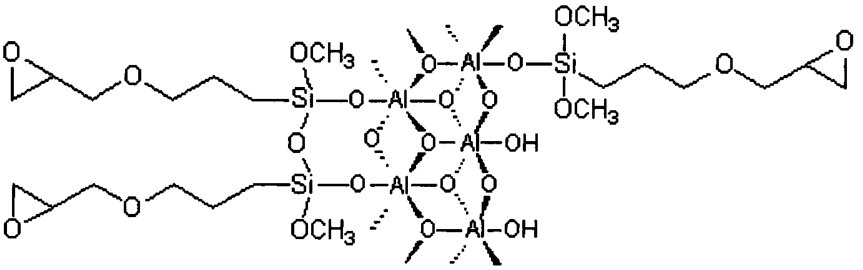
When preparing the multifunctional composites described by this patent, pre-curing the hybrid material is vitally important, prior to preparing the transparent composite.

In this process, the hybrid prepared in item 2 was placed in the kiln at a temperature of 50°C, until its volume was reduced by 40% (volume/volume). For example, for 1000 mL initially run through the curing process, 600 mL was obtained by the end of this process.

At the end of this process, the aged hybrid is ready for preparing the composite material.

Example 4: Preparation of composite material made from bacterial cellulose plus Boehmite – GPTS hybrid.

The Boehmite: 3-glycid oxypropyl trimethoxy silane (Boeh-GPTS) system was previously synthesized, as described in item 2. The resulting Boeh-GPTS system is presented in the structural representation shown below and was used for the preparation of optically transparent organic-inorganic bacterial cellulose hybrids.



There were subsequently obtained the Bacterial Cellulose (BC) composites plus Boehmite hybrid – GPTS using two routes:

I) The first route involves the dry BC membranes (DBC) with a variable average size of 1x1 to 100x100 cm^2, and an average thickness of 20 μm. The DBC membranes were dipped in stable suspensions originating from the reaction between the Bohemite and the 3-glycidyloxy-propyl trimethoxy–silane during a period of 24 hours, and were subsequently subjected to drying with the help of a mold similar to a frame, Figure 3, in an oven at 40 deg. C, for 12 hours. Depending on the desired application, the DBC/Boeh-GTPS composites may be obtained by overcoating onto one or two faces of DBC. The average thickness of the DBC/Boeh-GPTS composites with coating on both faces was 30 μm, containg the following ratio: 1:3 Boeh-GPTS.

II) The second route relates to the use of hydrated BC membranes (HBC) with a variable average size of 1x1 a 100x100 cm^2, and an approximate thickness of 4 mm. In order to remove the excess water present in the HBC (99%), the membranes were secured to the molds and were previously dried in an oven with an air flow at a temperature of 40 deg. C, for a period of 1 hour. After that period there was noted a decrease of about 70% of the initial volume of water present in the HBC. Subsequently the HBC membranes were carefully immersed in stable suspensions originating from the reaction between the Boehmite and the 3-glycidyloxy-propyl trimethoxy–silane during a period of 24 hours, and were subsequently subjected to drying with the help of a mold, in an oven at 40 deg. C, for 12 hours. The average thickness of the HBC/Boeh-GPTS composites was 70 μm.

Example 5: Characterization of the Optically Transparent Composites based on bacterial cellulose and boehmite, siloxane and/or a boehmite-siloxane system.

Irrespective of the methodology used for the preparation of the composites (dry route or hydrated route), the composites based on bacterial cellulose and on the Boeh-GPTS system were obtained in the fom of optically transparent membranes, macroscopically homogenous and flexible, such characteristics being desirable for a FOLED substrate.

In Figure 2 there are depicted the optical transmission spectra for a pure BC membrane, and the BC/Boe-GPTS composites. As may be clearly observed in the spectrum, the pure BC membrane exhibits poor optical transmission (around 40% at the visible spectrum region), while the DBC/Boeh-GPTS and HBC/Boeh-GPTS composites exhibit transparency values of 90% and 80%, respectively. It has been surprisingly noted that notwithstanding the high nanofibers content, the os BC/Boeh-GPTS Composites maintain a high degree of transparency, as shown in Table 1.

Table 1 – Transmittance Values at 550 nm for all the sample having been studied.

Sample	(%) Transparency (550 nm)

BC	40
Boeh-GPTS System	93
DBC/Boeh-GPTS COMPOSITE	90
HBC/Boeh-GPTS COMPOSITE	80

These results suggest the predominance of the effect derived from the size of the BC nanofibers, that are one hundred times smaller than the wavelength at the visible region of the electromagnetic spectrum, and for that motive are practically free from light scattering.

In spite of the excellent transparency, there is noted a small loss in optical transmission of the composites when compared with the pure Boeh-GPTS system. It is well established in the literature that nanocomposite materials undergo an increase in light scattering, resulting in loss of transparency. This behavior has been attributed to the difference in the refraction index (RI) of the elements that make up the nanocomposites. For example, the DBC/Boeh-GPTS composite exhibits a small loss of transparency, of 3%, while the HBC/Boeh-GPTS composite exhibits a loss of transparency of 11%. The RI value of the BC is 1.618 along the fibers and 1.544 crosswise, while the RI value of the Boeh-GPTS system is 1.466 to 543 nm and 21 deg. C. Nevertheless, the resulting BC/Boeh-GPTS composites are more transparent than pure BC, and have a refraction index of 1.489 to 543 nm and 21 deg. C, a value that is close to that which is observed for the Boeh-GPTS system, thus suggesting that the transmittance of the BC/Boeh-GPTS composites is mainly correlated to the Boeh-GPTS system. The difference in optical transmission of the BC/Boeh-GPTS composites can be attributed, mostly, to the presence of water in the interstitial spaces of the HBC/Boe-GPTS composite.

Example 6: Morphological characterization of the BC/Boeh-GTPS composites.

In Figure 3 there are shown Scanning Electron Microscopy (SEM) images obtained for dry BC membranes and for the BC/Boe-GPTS composites, respectively.

In Figure 3(a) there is depicted the nanometric fibers structure of the BC. In Figure 3(b) there is shown an image of the surface of the HBC/Boeh-GPTS composite. The image shows a homogenous coating of the BC microfibrils by the Boeh-GPTS system, resulting in a surface that is smooth, dense and practically devoid of defects.

Figures 3(c-f) refer to cross-sectional images of the DBC/Boeh-GPTS and HBC/Boeh-GPTS composites, respectively.

Figures 3(c) and 3(e) refer to the DBC/Boeh-GPTS composites deposited on both faces of the DBC, while Figure 3(d) shows a DBC/Boe-GPTS composite wherein only one face of the DBC is coated.

In Figures 3(c) and (e) it can be clearly noted that the Boeh-GPTS system only coats BC microfibers without penetrating the BC interstices. In point of fact, there may be observed the BC at the center of the composite, and in a structure which may be compared to a "sandwich", that is, coated on both faces by the Boeh-GPTS system. On the other hand, in Figure 3(d) there is disclosed the possibility of assembling a composite layer by layer, wherein one face refers to DBC and the other refers to the Boeh-GPTS system. This is an extremely interesting approach, particularly when a biocompatible interface is required. This is due to the fact that in those composites the BC interface may remain intact, allowing the use thereof for Medical purposes as a temporary skin substitute or even for the preparation of therapeutic transparent contact lenses. Figure 3(f) shows a sectional image of the HBC/Boeh-GPTS composite. The image reveals that, differently from the DBC/Boeh-GPTS composites wherein the coating of the BC occurs merely on the surface, in the HBC/Boeh-GPTS composites the Boe-GPTS system is capable of penetrating and filling the pores present in the hydrated BC membrane, in addition to also coating the surface of the BC.

Example 7: Structural characterization of the BC/Boeh-GTPS composites.

In Figure 4 there are presented X-Ray Diffractometry results for the BC, for the Boeh-GPTS system, and for the BC/Boeh-GPTS composites. Similarly to the PC, the BC is constituted by cellulose I. The BC exhibits two wide peaks at 15° and 22.5° approximately. Each peak exhibits a contribution of the diffractions corresponding to phases $I\alpha$ e $I\beta$, due to the overlaying of the reflections of planes $100_{I\alpha}$, $110_{I\beta}$ and $010_{I\alpha}$ (110) at 15° and of planes $110_{I\alpha}$ and $200_{I\beta}$ (200) at 22.5° (overlay).

The peaks denoted with (**) are attributed to the boehmite in phase γ-AlOOH (JCPD no. 21-1307), and may be partially covered due to the contribution of the allomorphous peaks of the siloxane group GPTS). All the BC/Boeh-GPTS composites exhibit peaks that are characteristic of the BC and of the Boeh-GPTS system at the 4-70 degrees region. There are no relevant alterations in the profile of the diffraction peaks of the DBC/Boeh-GPTS composites when compared to pure BC. However, for the HBC/Boeh-GPTS composite, the diffractogram discloses a pronounced decrease in the peak at 15°. This behavior may be associated to strong interactions between the Boeh-GPTS system and the BC, which could be restricting the orientation of the plane (110) during the drying process. As a consequence thereof the peak (110) of the HBC/Boeh-GPTS composite is much smaller than the peak present in the pure BC membrane.

Example 8: Thermal characterization of the BC/Boeh-GTPS composites.

In Figures 5 and 6 there are shown the TG/DTG and DSC curves for the BC samples, for the Boeh-GPTS system and for the BC/Boeh-GPTS Composites, respectively.

The bacterial cellulose exhibits a loss of mass of approximately 5% at the temperature range between 45 and 150 deg. C. That loss of mass is confirmed by an endothermic event observed to occur in the DSC curve, and may be attributed to the dehydration of the BC, such as, for example, by evaporation of the adsorbed water. A very intense event with great loss of mass (approximately 65%) is observed within the range of temperatures that comprises the interval between 250 deg. C and 400 deg. C., and with a maximum value at 355 deg. C as indicated in the DGT curve. That event was also observed in the DSC curve by way of an exothermic peak with a maximum value at approximately 350 deg. C, which is related to processes of degradation of the cellulose, such as depolymerization and subsequent decomposition of the glycoside units, followed by the formation of carbonaceous traces.

The thermal decomposition of the boehmite-siloxane system is characterized by three important events. The first two steps (30 to 250 °C) with mass loss of about 20 %, correspond to the dehydration of the adsorbed physically water molecules, as well as chemically bonded water molecules. These events were supported by two endothermic peaks present in the DSC curve, located at 105 and 190 °C. The following event which occurs between 260-600 °C, with mass loss of about 30 %, can be attributed to simultaneous events, such as the removal of chemically bonded water molecules, decomposition or organic compounds arising from start-up alkoxide, decomposition of the boehmite in alumina, followed by the subsequent surface dehydroxylation of the alumina. A rather wide exothermic peak, noted in the DSC curve, with a maximum of 390 °C confirms the events described in the TG curve.

For the CB/Boeh-GPTS composites, four main events are noted. The first two between 30-250 °C with mass loss of about 20% correspond to the evaporation of surface water and the loss of chemically bonded water molecules. These events were clearly noted in the DSC curve with the presence of two endothermic peaks at about 90 and 190 °C.

In the temperature range between 260-600°C an accentuated loss of mass is noted. For the CBS/Boeh-GPTS composite of about 50% and for the CBH/Boeh-GPTS composite 40%, these events refer to the decomposition of the CB, followed by simultaneous events deriving from the Boeh-GPTS system, as described previously. As revealed in the TG curve, there is a difference in the residue of the CB/Boeh-GPTS composites, suggesting that the CBH/Boeh-GPTS composite has a greater concentration of the Boeh-GPTS system.

The TG/DTG and DSC curves indicate that the CB/Boeh-GPTS composites present excellent thermal properties, and that there was no significant changes in the thermal stability of the CB with the presence of the Boeh-GPTS system. The onset temperature (T_{onset}) was highlighted in the curves with the assistance of the DTGs curves. A small decrease is generally noted in the T_{onset} for the CBS/Boeh-GPTS composite of about 7 °C, while the CBH/Boeh-GPTS composite presents a decrease of about 13 °C. This decrease may occur due to the breakages in the hydrogen bonds of the CB by owing to presence of the composite system.

Lastly, oxygen transmission rate measurements for the CBH/Boeh-GPTS composite reveal a drastic reduction in the oxygen diffusion of the pure CB (1320 mL/m^2/day) to (28.83 mL/m^2/day) for the CBH/Boe-GPTS composite. This result is of extreme relevance for the preparation of the FOLEDs.

Example 9: Mechanical assays using CB/Boeh-GTPS composites.

Figure 7 presents curves typical of Tension X Deformation for the CB membrane and the CB/Boeh-GPTS composites. Due to the great fragility, it was not possible to prepare self-supporting films of the Boeh-GPTS system.

CB membranes present good mechanical properties. Additionally, a high resistance was noted for materials derived from CB, chiefly due to their nanofiber network structure and to the high performance of the nanofibers.

In fact, values for the tension and deformation module extracted from mono filaments of CB have been evaluated by means of AFM and RAMAN measurements, which reveal values of 78 GPa and 114 GPa, respectively. The curve obtained for the pure CB membrane presents an initial linear behavior followed by a plastic behavior. The Young module value obtained from the linear part of the curve is 12.5 GPa, and is in accordance with results from literature. The rupture tension for CB is 112.5 MPa, whereas elongation is 1.5%.

Different mechanical behaviors were noted for the CB composites obtained from CBS and from CBH.

A reasonable decrease was noted in the mechanical properties of the CBS/Boeh-GPTS composite. The maximum tension determined was 50.5 MPa, revealing a reduction of over fifty percent in this same property in the pure CB. The Young module was also substantially lower (2.8 GPa), that is, at least four times lower compared to pure CB. In contrast, there was an increase in the elongation to 2.5%. Although the results obtained for the CBS/Boeh-GPTS composite were relatively less than pure CB, they reveal an important aspect. As mentioned previously, the Boeh-GPTS system is not capable of forming self-supporting films, and in this case the nanofiber network of the CB acted efficiently as reinforcement in achieving transparent, flexible and thermally stable films. Additionally, the values for tension, deformation and Young Module of the CBS/Boeh-GPTS composite are comparable to various other organic polymers.

The CBH/Boeh-GPTS composite presented values for maximum tension and Young module higher than pure CB, in the amounts of 116 MPa and 13.7 GPa, respectively, while elongation was similar to pure a CB (1.3%).

The increase in the mechanical properties of the CBH/Boeh-GPTS composite can be attributed to strong interactions which occurred between the CB and the Boeh-GPTS system.

It can also be inferred that the methodology applied in preparing the

CB/Boeh-GPTS composites is a determining factor in its mechanical properties. Whereas the CBS/Boeh-GPTS hybrid composite is formed only by surface covering of the Boeh-GPTS system, in the CBH/Boeh-GPTS composite there is a more effective interaction between the CB and the Boeh-GPTS system. In this methodology, the hydrated CB membrane has a porous structure that permits diffusion of the Boeh-GPTS system to the inside of its interstices. Moreover, the water molecules present inside the CBH/Boeh-GPTS composite are acting as plastifying agent leading to the formulation of hydrogen bonds between the CB hydroxyls, the water and the Boeh-GPTS system.

CLAIMS

1) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** CHARACTERIZED BY containing a bacterial cellulose membrane and an inorganic hybrid.

2) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 1, CHARACTERIZED WHEREIN the inorganic hybrid is a compound of Boehmite: 3-glycidiloxy-propyl trimethoxy–silane (Boeh-GPTS).

3) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 1, CHARACTERIZED BY containing transparency of 70 to 100 %.

4) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 1, CHARACTERIZED WHEREIN the bacterial cellulose membrane is chosen from the group comprised by: dry bacterial cellulose membrane (CBS) and hydrated bacterial cellulose membrane (CBH).

5) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 2, CHARACTERIZED BY the fact that the Al:Si ratio in the hybrid Boeh-GTPS is comprised between 0.01 mol : 1 mol and 100 mol : 1 mol.

6) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 4, CHARACTERIZED WHEREIN the CBS has a thickness preferably between 0.1 and 15 mm.

7) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 4, CHARACTERIZED WHEREIN the CBH has a thickness preferably between 1 and 1500 µm.

8) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 2, CHARACTERIZED WHEREIN the Boeh-GTPS solution presents a concentration of 1 to 5 M.

9) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claims 1 to 8, CHARACTERIZED WHEREIN the bacterial cellulose membrane is covered on at least one of its surfaces by the Boeh-GTPS hybrid.

10) **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL**

CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM, according to claims 1 to 8, CHARACTERIZED WHEREIN the Boeh-GTPS hybrid is incorporated into the pores of the bacterial cellulose membrane.

11) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** CHARACTERIZED BY containing at least one of the following steps:

i. Production of bacterial cellulose membrane (CB);
ii. Drying of bacterial cellulose membrane (CB);
iii. Preparing the Boehmite (Boeh) solution;
iv. Preparing the 3-glycidiloxy-propyl trimethoxy–silane (GTPS) solution;
v. Preparing the Boeh-GTPS hybrid;
vi. Curing the Boeh-GTPS hybrid;
vii. Immersing the CB in Boeh-GTPS solution; and
viii. Drying the CB/Boeh-GTPS composite.

12) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 11, CHARACTERIZED WHEREIN the drying of bacterial cellulose membrane occurs in a greenhouse with airflow, at a temperature of 40 °C, over a period of 1 to 24 h.

13) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 11, CHARACTERIZED WHEREIN the curing of the Boeh-GTPS hybrid occurs in a greenhouse at a temperature of 50 °C.

14) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 13, CHARACTERIZED BY the occurrence of a reduction of 40 % in the volume of the Boeh-GTPS hybrid.

15) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 11, CHARACTERIZED WHEREIN the immersion of CB into a solution of the Boeh-GTPS hybrid occurs for a period of 24 h.

16) A process of obtaining **OPTICALLY TRANSPARENT COMPOSITES BASED ON BACTERIAL CELLULOSE AND BOEHMITE, SILOXANE AND/OR BOEHMITE-SILOXANE SYSTEM,** according to claim 11, CHARACTERIZED WHEREIN the drying of the CB/Boeh-GTPS composite occurs in a greenhouse at a temperature of 40 °C for 12 h.

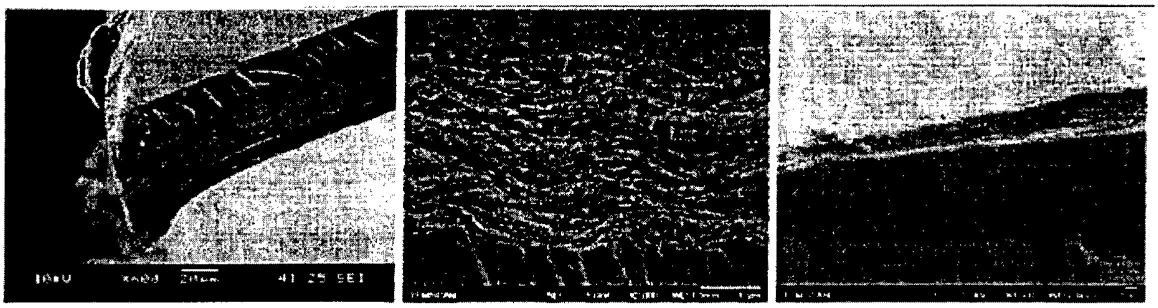


FIGURA 1

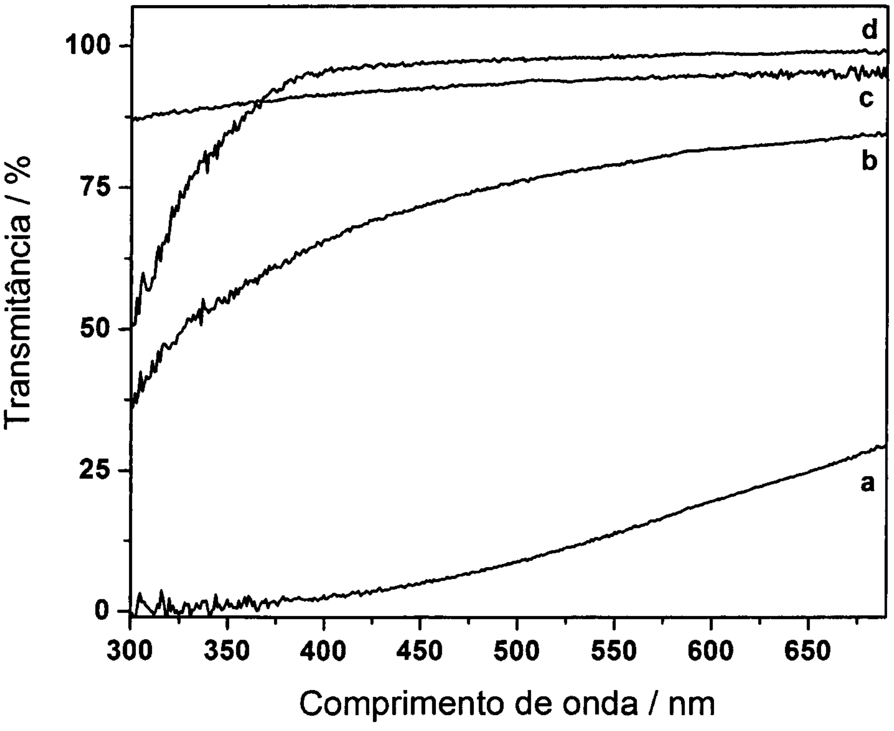


FIGURA 2

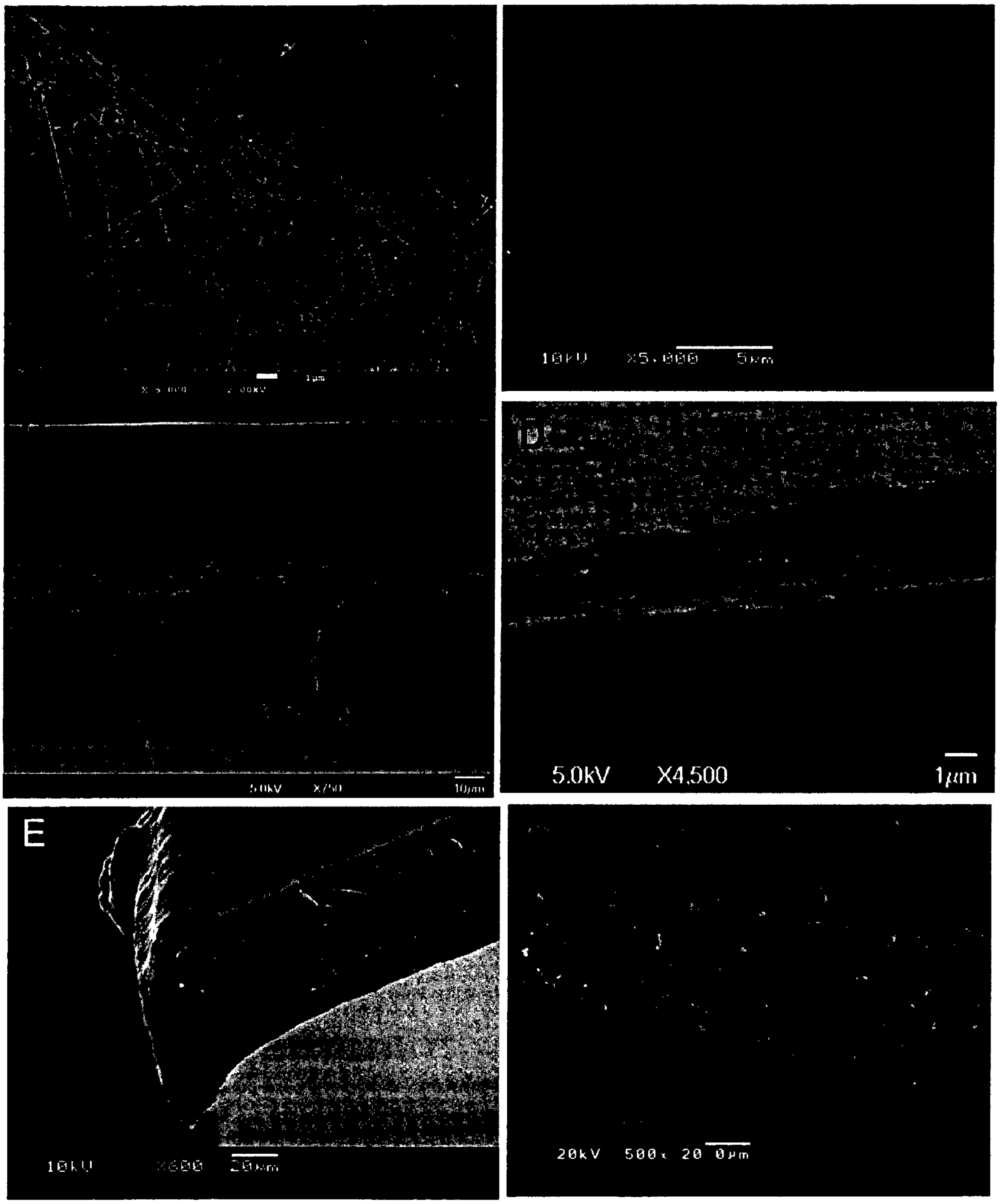

X5,000
2.00kV
1µm
10kV X5,000 5µm
5.0kV X750 10µm
D
5.0kV X4,500 1µm
E
10kV X600 20µm
20kV 500x 20 0µm

FIGURA 3

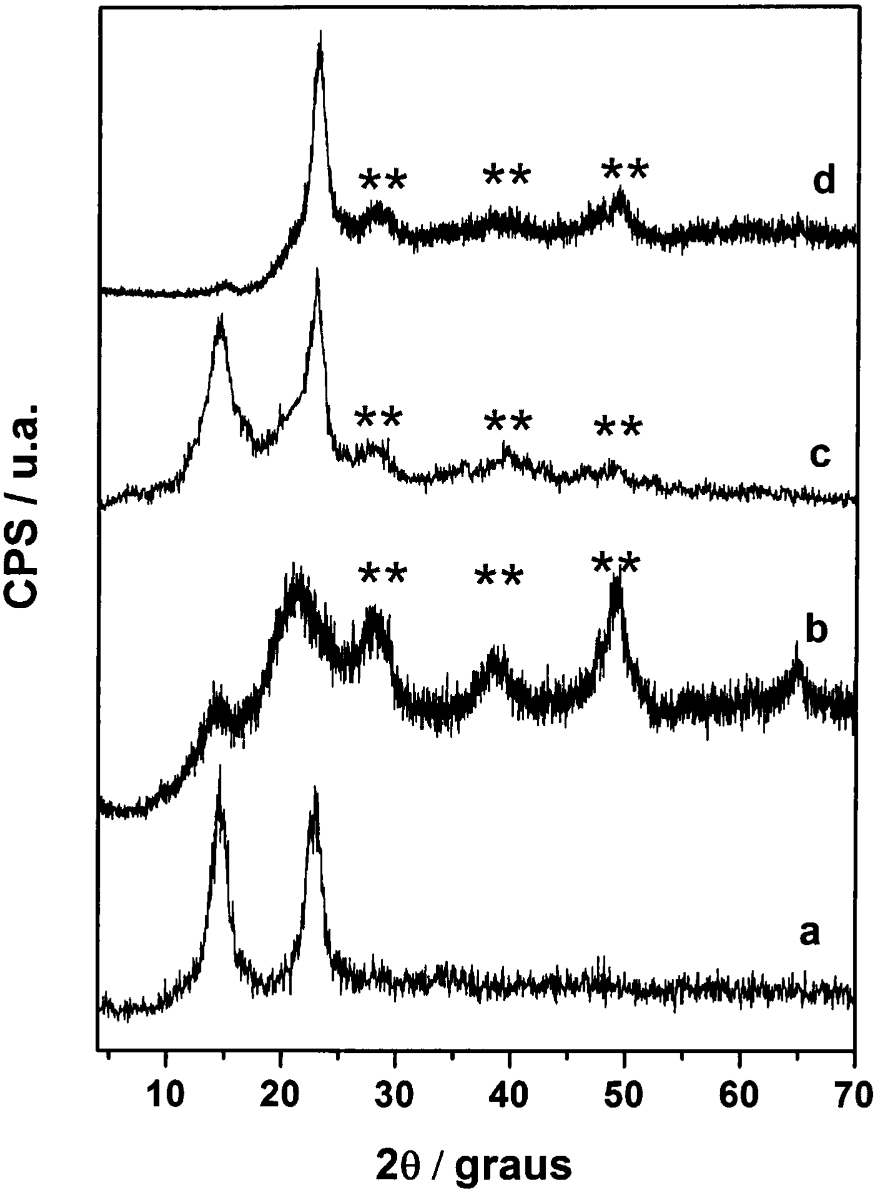


FIGURA 4

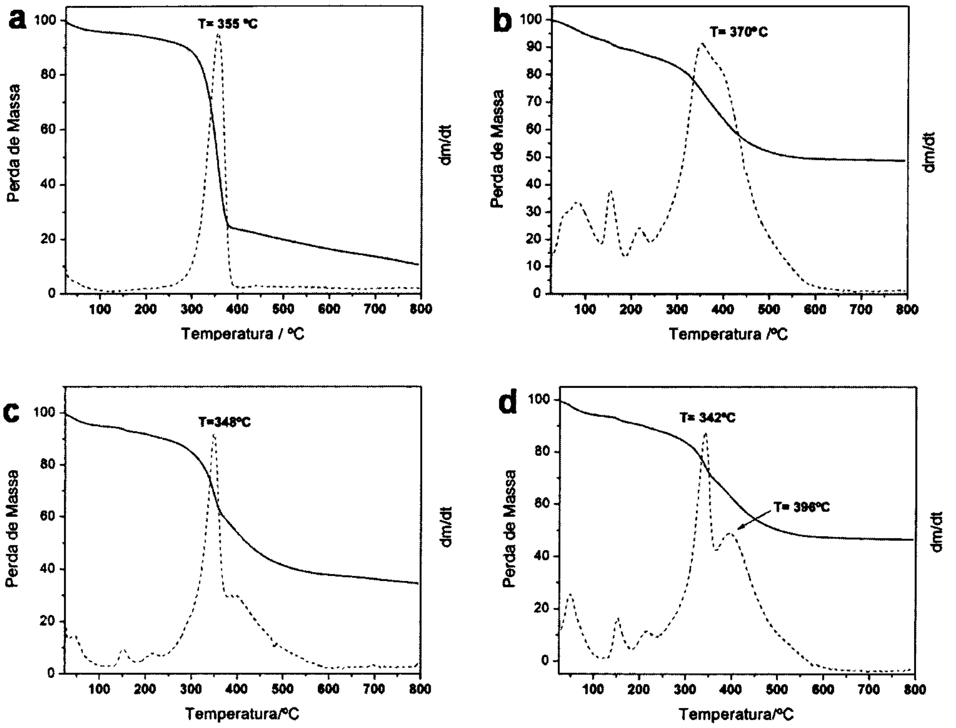

a
T= 355 °C
Perda de Massa
dm/dt
0
20
40
60
80
100
100 200 300 400 500 600 700 800
Temperatura / °C
b
T= 370°C
Perda de Massa
dm/dt
0 10 20 30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800
Temperatura /°C
c
T=348°C
Perda de Massa
dm/dt
0
20
40
60
80
100
100 200 300 400 500 600 700 800
Temperatura/°C
d
T= 342°C
T= 396°C
Perda de Massa
dm/dt
0
20
40
60
80
100
100 200 300 400 500 600 700 800
Temperatura/°C

FIGURA 5

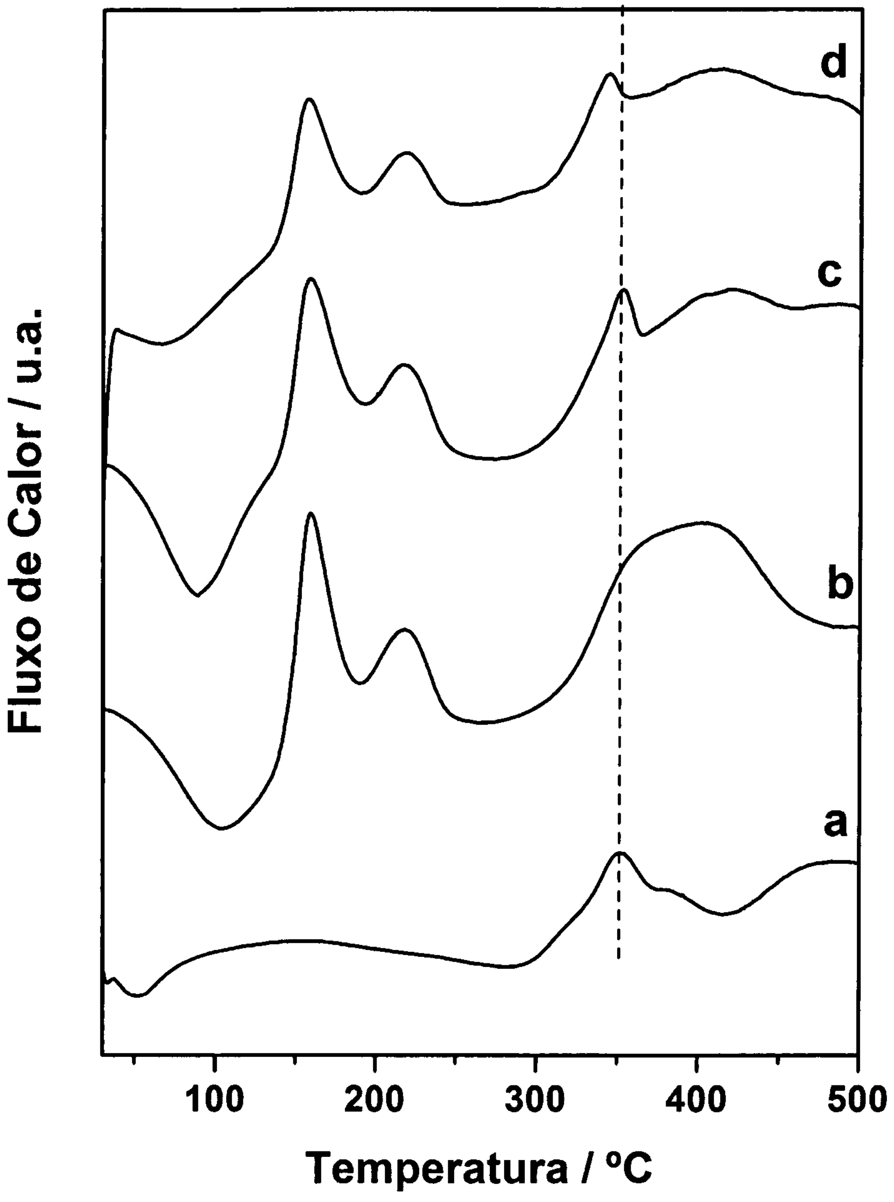


FIGURA 6

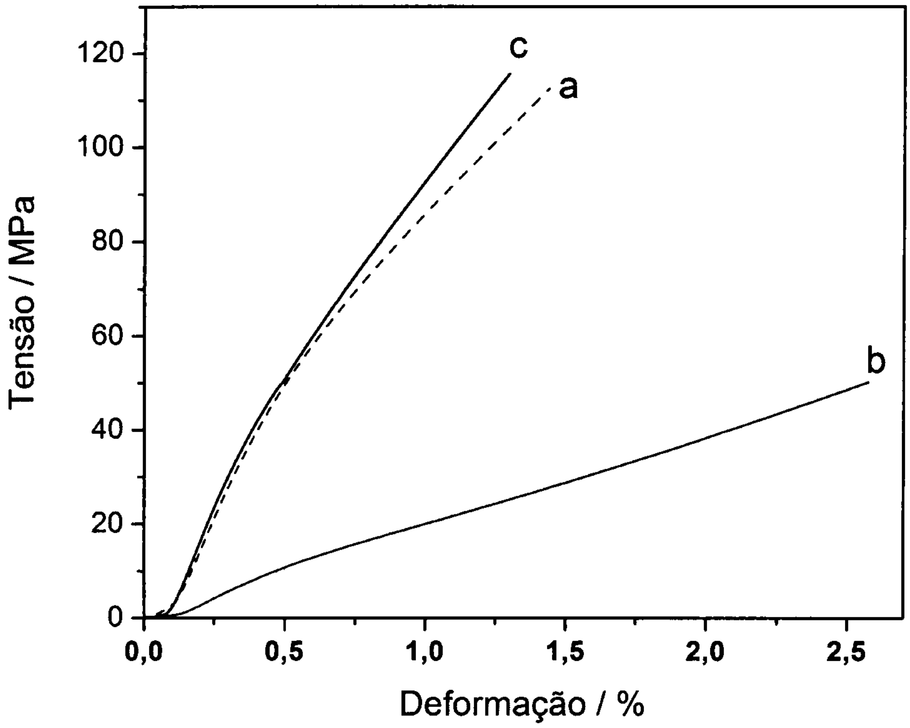


FIGURA 7

INTERNATIONAL SEARCH REPORT

International application N°
PCT/BR2012/000024

A. CLASSIFICATION OF SUBJECT MATTER

C08L1/02 (2006.01), C08K3/22 (2006.01), C08K5/5419 (2006.01)

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)

C08L 1/00, C08K3/00, C08K5/00

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

INPI DATA BASE - BRAZIL

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC , USPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claims N°
A	EP 2042300 A1 (PIONEER CORP [JP]) 01 April 2009 (2009-04-01) the whole document	1-16
A	US 7485720 B2 (ASAHI CHEMICAL IND [JP]) 03 February 2009 (2009-02-03) abstract, column 2, lines 49- 55, column 7, lines 29-32, column 8, line 16	1-16
A	US 2009298976 A1 03 December 2009 (2009-12-03) the whole document	1-16

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

* Special categories of cited documents:

"A" document defining state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to stablish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority claimed

"T" later document published after the internationa filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"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 obvius to a person skilled in the art

"&" document member ot the same patent family

Date of the actual completion of the international search **22/05/2012**	Date of mailing of the international search report 250512
Name and mailing address of the ISA/**BR** INPI INSTITUTO NACIONAL DA PROPRIEDADE INDUSTRIAL Rua Sao Bento nº 1, 17º andar cep: 20090-010, Centro - Rio de Janeiro/RJ Facsimile N°. +55 21 3037-3663	Authorized officer **Julia Candida Afonso Martins** Telephone N°. +55 21 3037-3493/3742

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application N°

PCT/BR2012/000024

Patent documents cited in search report	Publication date	Patent family members	Publication date
EP 2042300 A1	2009-04-01	CN 101489783 A	2009-07-22
		EP 2042300 A4	2009-10-14
		JP 2008024778 A	2008-02-07
		KR 20090029845 A	2009-03-23
		TW 200827392 A	2008-07-01
		US 2009305033 A1	2009-12-10
		WO 2008010449 A1	2008-01-24
US 7485720 B2	2009-02-03	CN 1602318 A	2005-03-30
		CN 1288167 C	2006-12-06
		DE 10297399 B4	2010-08-26
		JP 4393193 B2	2010-01-06
		US 2004267006 A1	2004-12-30
		WO 03040189 A1	2003-05-15
US 2009298976 A1	2009-12-03	CN 101297000 A	2008-10-29
		JP 2007146143 A	2007-06-14
		WO 2007049666 A1	2007-05-03