

Research Article

Laminated, Composite and Sandwich Membranes Based on Graphene-Oxide with Nano-Textiles

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Abstract

The contribution describes preparation of graphene-oxide suspensions and their hybrid compounds, GO-biochar, $GO-C_{en}$, $GO-CF_{n,a}$, which are subsequently applied to nano-textiles using various techniques. This method was used to prepare composite and sandwich-type films or laminated nano-textiles. Relative arrangement in product (film) crosssections was identified in products prepared using SEM analysis. Thermal stability of the products was determined using DTA, DSC analysis and compared to the stability of the nano-textiles. Chemical properties of graphene- oxide (GO) allow a number of its modifications, partial reduction, creation of composites with metals and their oxides. Preparation and thermal analysis GO-TiO,/ PCI /GO-TiO, has been described as an example. The conclusion of the project suggests possible application of the products (films).

Keywords: Nano-Textiles; Composite; Graphene

Introduction

GO membranes laminar, layered with have structure functional oxygenous epoxy, carboxyl, carbonyl or hydroxide groups, which induce the hydrophilic character of sp³ C-O (approx. 40%), while also containing the hydrophobic component sp²C=O [1].

There are possibilities of preparation for these membranes [1] such as smearing a drop of GO colloidal suspension over a smooth surface (SiO₂, polymer, paper etc.) via spray, vacuum filtering or the Langmuir-Blodgett method. GO membranes can only exist as a free-standing C-frame deposited either onto a different membrane and functionally connected with a polymer or modified into an "in situ" polymer matrix, creating a non-covalent or covalent composite connection [2-5], or onto a porous material [6-9].

Up until a certain level, the GO oxygenous functional group can be de-oxidized depending on the used reducing agent, preparing a compound that is commonly known in literature as rGO. This compound has increased thermal stability, hydrophobic character and increased capability of π - π interactions and defect (pore) creation within the carbonaceous grid frame. Graphene itself is a mono-atomic layer of carbon, undissolvable for any gases or solutions, while GO (rGO) with controlled defects exhibits great potential for application in filtering technology. For graphene, pores are purposefully created in the C-grid using directed electron rays, ion oxidization etching or oxygenous plasma. Pore size and acquired shape are published in the graphic concept [5,10]. Pore size and shape subsequently influence the application in Figure 1 [11], which shows the different progression of gas/ion separation for GO and graphene. Membranes based on graphene, GO, rGO are applied in the area of molecular separation, both in selective separation of gases, ions, small and ultra-small particles, desalination and purification of water, including disinfection [4,6,7,12-17].

The results of gas and ion separation are influenced by diffusion speed [18], layer investing [19], spacing between nano-particles of GO providing channels (Figure 1), gap size between the layers. The functional groups also expand separation abilities and possibilities. Examples of selective separation: CH₄/CO₂, CH₄/H₂S, CH₄/N₂, H₂/CO₂







Figure 2: a) lamination and nanotextiles, b) composite.

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[9,20-23]. Graphene-based films have been finding application thanks to their filtering capabilities, as well as other application as adsorption materials, battery electrodes, super-capacitors, photo-catalysis, antibacterial materials and moisture sensors, organic and biological substances. Some of the application will be tested in the experimental part conc. adsorptive capabilities of GO, biochar and GO-Biochar films.

Experimental Part

GO is acquired by means of Hummers graphite oxidization (1958), e.g. via oxidation mixture of $KMnO_4 + NaNO_3 + H_2SO_4$. Once the mixture is dissolved using water, HCl and $30\% H_2O_2$, solution, repeated decanting and skimming yields a water suspension with negative reaction to sulphate ions. By regulating the skimming time and speed, a certain consistency of the suspension can be achieved, which allows for variants when applying onto nano-textiles (see below).

The same procedure was used to oxidize graphite together with $\mathrm{C}_{_{\!\!60}\!},$ CF_{0.9} fluorine-graphite and post-biomass pyrolysis compounds -biochar in various mass ratios, most often 2:1 in favour of graphite. This led to creation of hybrid compounds of GO $\text{-}\mathrm{C}_{_{60}}$, GO -CF, GO -biochar, which were able to create a film, membrane. These prepared suspensions of hybrid compounds and GO were applied onto the nano-textiles using a spatula, mechanical smearing or aerosol dispersion. Depending on the suspension consistency, this resulted in lamellar/composite arrangement (nano-textiles between GO layers) or a sandwich arrangement, i.e. layer alternation (nano-textile-GO-nanotextile) -see the illustrative in Figure 2. This allows for a wide range of variants, e.g. application of another GO layer, alternating nano-textile types. Further variation is provided by changing the level of meshing of the nanofibers in the nano-textiles. This also influences the level of adsorption on the surface or permeation through the textile. This is always followed up by drying at a temperature gradually increasing from 25 to 70°C. For application in photo-catalysis, composite of GO-TiO₂/PCL/GO-TiO₂ was also created, along with a sandwich where steel micro-fibers were inserted into the GO suspension with the goal of getting a film capable of shielding against magnetic radiation.

Graphite oxidization- GO preparation

3 g of graphite have been re-layered in the Erlenmeyer flask using 65 ml of concentrated H_2SO_4 with 4 g of NaNO₃ added. The mixture was stirred using a magnetic stirrer and cooled down to 7–10°C. Afterwards 7 g of KMnO₄ was gradually added and the mixture was gradually heated up to laboratory temperature, which was gradually increased to 50-66°C. At this temperature, the condensing reaction mixture was stirred for 4 hours. The mixture was then left overnight at laboratory temperature, followed by adding 40 ml HCl and 40 ml 30% H_2O_2 into the flask and stirring the mixture for 1 hour. This was followed by decomposition (reaction) and final addition of 150 ml of distilled water. The mixture was skimmed and the acidic water part decanted. As a final step, 100 ml more of distilled water was added. This process was repeated 20 times until a negative reaction to sulphate ions was achieved.

Oxidization of graphite and biochar

1.22 g of biochar and 1.7 g of graphite have been re-layered in the Erlenmeyer flask using 40 ml of H_2SO_4 with 20 ml of HNO_3 . The mixture was cooled down to 7-10°C (stirred using a magnetic stirrer). 20 g of KClO₃ was then gradually added during intense stirring. The mixture was gradually heated up to laboratory temperature, which was gradually increased to 50–60°C. At this temperature, the mixture was subjected to intense stirring for 4 hours. The resulting reaction mixture

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was left for 4 days at laboratory temperature. 100 ml of distilled water, 40 ml of HCl and 40 ml of H₂O was then added. The prepared acidic mixture was skimmed and the acidic water portion was decanted. Another 100 ml of distilled water was added and the skimming and decanting process was repeated 20 times until a negative reaction to sulphate ions was achieved. The processes were performed at the same reaction conditions as for biochar, also for C_{60} , CF_{0.0}.

GO-TiO2 composite

44 mg of nano TiO_2 was added into the Erlenmeyer flask with 8 ml of dense suspension of GO. The mixture was alternately sonified and stirred. The content of the flask had become denser (a brown, mushy matter), so much that it was necessary to add 40 ml of H₂O and stir and sonify at 40°C for 4 hours. Once cooled, the suspension was applied onto PCL nano-textiles. The prepared films were gradually dried at 25–70°C for 16 hours.



Steel micro-fibres (provided by the Technical University in Liberec)

$$\begin{array}{c} \begin{pmatrix} \mathbf{H} & \mathbf{H} & \mathbf{O} & \mathbf{O} \\ \mathbf{I} & \mathbf{I} & \mathbf{I} & \mathbf{I} \\ \mathbf{N} - (\mathbf{CH}_2)_6 - \mathbf{N} - \mathbf{C} - (\mathbf{CH}_2)_4 - \mathbf{C} \end{pmatrix}_n \\ \textbf{Nylon 66} \\ \hline \begin{pmatrix} \mathbf{H} & \mathbf{O} \\ \mathbf{I} & \mathbf{O} \\ \mathbf{N} - (\mathbf{CH}_2)_5 - \mathbf{C} \end{pmatrix}_n \\ \textbf{Nylon 6} \end{array}$$

PA6 polyamide

Polymer nanofibers were prepared at the Technical University in Liberec using the "Nanospider" technology. These fibers were applied onto the polypropylene surface within the nano-textile mold.

Used chemical compounds -nano TiO_2 made by Sigma Aldrych, biochar -biomass pyrolysis product (Biouhel.cz s.r.o., Zlín) C₁₄O, 2% soiled by salts of Si, Al, K, Ca, Mg.

Device equipment

SEM analysis: FEI Quanta 650 FEG scanning electron microscope (FEI, USA)

TGA /DSC, 2 Metter Toledo

Results and Discussion

As already stated in the experimental section, the described procedure enables a variety of modifications in the combination of GO and its hybrid compounds with nano-textiles, depending on the method by which the suspension is applied, its consistency and type and structure of nanofibers in the applied nano-textile. The procedure allows mechanical modifications (steel fibers together with GO between layers of PCL) and chemical modifications (nTiO₂). The size of the applied layers of GO and its hybrids was monitored via change of mass, including a following re-calculation to the area unit of the nanotextile or cut thickness (Figures 3-9). SEM images were not taken for sections of the pure nano- textiles (PCl, PA6) only in the case of hybrid modification. In addition to the SEM analysis, TGA and DSC analyses were used to determine the thermal stability in order to provide application safety.

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Figure 3: Sections of PCL nano-textile contact with GO applied (nano-textile lamination).



Figure 4: Section and structure of product surface I (PA6/GO/PA6) – sandwich.



Figure 5: Section and structure of product II (GO-biochar/PCL/GO-biochar) - composite.



Figure 6: Section and structure of product surface IIII (GO/PCL/GO).



Figure 7: Section and structure of IGO-TiO₂/PCL/GO-TiO₂ surfacecomposite.



Figure 8: Section and structure of product surface IIII (GO/PCL/GO).



Figure 9: Section and structure of ${\rm GO-TiO_2/PCL/GO-TiO_2}$ surface-composite.

The next section shows pictures of sections and surfaces of selected film. The important property here is thermal resistance, which is presented by the TGA and DSC analysis curves.

Thermal analysis of default precursors

Thermal Analysis of precursors has been described through the Graph from Figures 10-13.

Thermal analysis result comparison -PA6/GO/PA6 sandwich against PA6 nano-textile (I)

Note the decomposition progression for the sandwich in Figure 14, where exo-effects are evenly alternated by endo-effect at temperatures from 150°C upwards, with the highest weight loss throughout the endo-effect progression. The entire sandwich decomposition ends in an exo-effect, peaking at 567°C with weight loss of 25%.

The decomposition of the PA6 nano-textile itself takes place from 150°C to 285°C in a protracted endo-effect and a 23% weight loss. The greatest weight loss (39%) also occurs during an endo-effect at 430°C. There are two endo-effects on the curve Figure 12, the first one at 384°C with a 6% weight loss and the second one with main maximum at 515°C and weight loss of 19%. The GO influence manifested in warmer change







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of the sandwich decomposition. The first and the last exo-effect in the sandwich are affected by the GO decomposition exo-effect. Mutual influence of these components is obvious in the created sandwich arrangement from the comparison of shape and progression of the TGA and DSL curves for the sandwiches with GO and nano-textiles.

Composite thermal analysis result comparison for GObiochar/PCL/GO-biochar (II)

The measurement thermograph (Figure 15) was divided into three blocks within the range of $254-630^{\circ}$ C -b), c) and d) with continuous exo-thermal change. Block b) peaks at 268° C, block c) ranges from 330 to 510° C with three hints of peaks and the high peak of the exo-effect was in block d) at 622° C. The highest weight loss (58 %) of the thermal decomposition has shown in block c).

The PCL decomposition itself happened in the thermal range of 260– 580°C, with three identifiable exo-effects with maximums at 389°C, 410°C and 465°C. The main weight loss (73%) happened between the first and the second exo-effect (Figure 13). The PCL influence in the composite had mainly manifested in the protracted c) block. The hybrid compound effect had also manifested in block b), c) and partially d). When comparing the TGA and DSC of the starting components and the prepared composite, increased thermal stability can be clearly declared for the composite with a difference of 160°C, especially compared to the nano-textile.

Thermal analysis result comparison for the go/pcl/go (iii) composite and the caprolactam nano-textile

The measured thermograph was divided into three blocks in the temperature range of $150-600^{\circ}$ C -b), c) and d), with mean temperature of 220°C for block b), temperature range of 265–480°C for block c), and mean temperature of 571°C for block d) (Figure 16).

The PCL decomposition itself happened in thermal range of 260–580°C, with three identifiable exo-effects with maximums at 389°C, 419°C and 465°C (Figure 13). The main weight loss (73%) happened between the first and the second exo-effect. The PCL influence in the composite had mainly manifested in the protracted c) block.

Thermal stability of the composite had increased by 100°C compared to the nano-textile (PCL) and the thermal change of the range for the last exo-effect. 30°C for the composite, 100°C for PCL, which is why we can expect mutual physical or chemical influence between the polymer and GO.

Composite thermal analysis result comparison for GO-TiO₂/ PCL/GO-TiO₂

The comparison of thermograph curves for the GO/PCL/GO composite alone and composite containing TiO_2 has shown a difference in the thermal decomposition progression. The significant difference can be seen on the TGA curve in the last third of the decomposition (Figures 16-19). The decomposition of the TiO_2 composite starts ca. 30°C later and the maximum of the last exo-effect was 70°C lower; despite that the thermal change of the decomposition reaction of this exo-effect had doubled.

It is obvious that the TiO_2 content had played a part in the thermal properties of $\text{GO-TiO}_2/\text{PCL/GO-TiO}_2$. According to literature [23] TiO_2 is expected to be wrapped into plates of GO using hydroxy groups on the surface of GO leads to the Ti-O-C configuration.

Meltblown technology

A Meltblown technology was used to prepare a further type of sandwich arrangement between GO-Biochar and non-woven textiles. With this technology, polypropylene (PP) fabrics (Mostek) produced fiber



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Figure 17: TGA and DSC analysis of product GO-TiO₂/PCL/GO-TiO₂.



Figure 18: Prepared sandwich with biochar by Meltblown PP technology.

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fabrics, which were doped with powder GO, GO-Biochar (2:1) and the biochemistry itself. Subsequently this deposited fabric was coated with nanoparticle with PCl and laminated (Figure 16) (where is shown cut out of the prepared foil by *Meltblown* technology on the left which was further tested).

This prepared material was tested according to Czech Technical Standart CSN EN 149: 2002 + A1: 20009 Respiratory protective devices on the cuts with adsorbent of the doped parts and parts without adsorbent.

Specific measuring instruments:

- INSPEC breathing resistance test device;
- Sheffield head;
- Manometer GDH 200-07;
- Yokogawa P052 Rotameter;
- Yokogawa P161 Rotameter;
- Stopwatch Ruhla;
- Thermometer type Centigrade 0.1;
- LORENZ type BIA paraffin oil aerosol filter device;
- Aerosol NaCl Testing Unit, MOORE'S Type 1100;

Metrological provision

The metrological provision of the instruments is performed in accordance with the Research Laboratory of Occupational health and Safety- metrology regulations (VÚBP-Praha).

Test results of prepared membranes (Tables 1 and 2)

- 100% = ADF 62
- A, B = the samples with coating
- C = A sample without coating

160 -biochar

- 150 -GO-biochar
- 200 -GO

Best results against air resistance were achieved for the biochar membrane prepared by *meltblown* technology on non-woven fabrics from PP.

Conclusion

Products prepared using graphene oxide and its nano-textile hybrids (PCI, PA6) feature higher thermal stability than the default nano-textiles. Suspension consistence/ composition and nano-textile porousness can influence which connection is established and therefore which particular product is prepared. The mutual link and



Figure 19: Measurement device for respiratory resistance and aerosol penetration for NaCl and paraffin oil (b) Sodium chloride test - Breakthrough of NaCl after 3 minutes. Flow rate 45 l/min.

Sample	State	Resistance in Pa	
		During 30 l/min	During 95 l/min
200A-GO	AR	1925	-
200B-GO	AR	1844	4920
200C-GO	AR	6.5	39
160A- biochar	AR	2230	3820
160B-biochat	AR	2150	3930
160C-biochar	AR	3	33
150A-GO-biochar	AR	1965	2710
150B-GO-biochar	AR	1971	2820
150C-GO-biochar	AR	4	35

Note: Values 150, 160 and 200 in the table and following table indicate the weight of the powder (adsorbent) per m^2

 Table 1: Determination of respiratory resistances.

Sample	State	Penetration %
200B-GO	AR	<1 x 10 ⁻³
200C-GO	AR	98
160B-biochar	AR	<1 x 10 ⁻³
160C-biochar	AR	96
150B-GO-biochar	AR	<1 x 10 ⁻³
150C-GO-biochar	AR	99

(a) Paraffin oil test - Breakthrough of paraffin oil after 3 minutes, flow rate 95 I / min.

Sample	State	Penetration %
200A-GO	AR	0
200C-GO	AR	93.1
160A-biochar	AR	0
160C-biochar	AR	93.1
150A-GO-biochar	AR	0
150C-GO-biochar	AR	96.5

(b) Sodium chloride test - Breakthrough of NaCl after 3 minutes. Flow rate 45 I /min

Table 2: Determination of aerosol penetration.

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combination of components, along with further graphene oxide modification, provide high application flexibility namely in electrical engineering as a membrane or sensor material, as well as adsorption or anti-bacterial material. Article shows the potential application of GO, Biochar and hybrid GO-Biochar with PP microfibers as an adsorptive material for the measurement of the respiratory resistance and aerosol penetration for certain substances (NaCl, paraffin oil).

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