

MORPHOLOGICAL AND STRUCTURAL INVESTIGATION OF THE POLY(VINYL CHLORIDE) / GRAPHENE OXIDE COMPOSITES

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ABSTRACT. The morphological and structural properties of the poly(vinyl chloride)/graphene oxide (PVC/GO) composites are reported. By the mixture of the two constituents, the PVC/GO composite membranes with a concentration of the GO sheets varying from 0 wt.% to 0.5, 1, 2, 3, 4 and 5 wt.% were prepared. Using scanning electron microscopy (SEM) and the analysis of the atomic force microscopy (AFM) images we observed that as increasing the GO concentration in the PVC mass from 0 wt.% to 5 wt.%, the average surface roughness decreases from 235 μm to 227 μm . Using Raman scattering, we report that as increasing the GO concentration in the PVC mass, the ratio between the relative intensities of the Raman lines situated in the spectral ranges 600-650 and 2850-3000 cm^{-1} ($I_{600-650}/I_{2850-3000}$) increases as a consequence of the change of GO carbon atoms hybridization from sp^2 to sp^3 . An increase in the number of C-C bonds, simultaneous with the appearance of O-C=O bonds and the decrease of the chlorine concentration, when the GO concentration increases in the PVC weight is reported by X-ray photoelectron spectroscopy (XPS). The down-shift of the main diffraction signal from 24° to 26° when the GO concentration

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increases in the PVC/GO composite mass from 0 wt.% to 5 wt.%, confirms the incorporation of GO in the polymeric matrix and the modification of the original PVC sample structure. Using transmission electron microscopy (TEM), no agglomerations of the GO structures within the PVC/GO matrix contrast limit were observed.

Keywords: *poly(vinyl chloride), graphene oxide, membranes*

INTRODUCTION

Due to the ease of processing, low cost, good physical, chemical and corrosion properties, poly(vinyl chloride (PVC) is a widely used polymer. As estimated in the PVC market report [1], the global PVC market stood at US\$ 57.06 billion in 2015. It is expected a tremendous rise during the period from 2015 to 2021, the revenue in this PVC market reaching to US\$ 78.90 billion by the end of the forecasted period of time and it is forecast to increase even more to 88.02 Billion USD by 2027 [2]. The main available products in the PVC market are flexible and rigid PVC. The flexible PVC has applications in medical equipment, signage, electrical cable insulation, plumbing, and inflatable items, while rigid PVC is used across construction sectors. However, PVC has several disadvantages such as poor processability, thermal stability and weatherability. Moreover, PVC without plasticizers or fillers is typically brittle and is not suitable in many fields [3-5].

Recently, the improvement in thermal, electrical and mechanical properties of PVC matrix with graphene derivatives has been reported in many related papers [6-9]. As filler material, graphene oxide (GO) is inexpensive, it has hydrophilic character and it contains epoxy, alcohol, carbonyl and carboxyl groups [10, 11]. Additionally, GO can be homogeneously dispersed in organic solvents such as tetrahydrofuran (THF) and N,N'-dimethylformamide (DMF), which allows a good interfacial adhesion between polymer and GO, also inducing significant changes to the composite properties. Due to the lone pairs of electrons at the chlorine atom of the PVC, and respectively the dipole-dipole interaction between hydrogen and chlorine atom which can stiffen the polymer backbone, the PVC/GO composites are of particular interest. In addition, GO can interact with PVC chlorine atoms and become an active site that allows anchoring of other functional groups thus improving the properties of the composite. Deshmukh and Joshi [7] reported that the strong interaction between PVC and GO increased thermal stability of the composites.

The objective of this work is to prepare PVC/GO composite membranes by mixing of GO with PVC dissolved in THF and DMF. The morphological and structural characteristics of the PVC/GO composites were investigated.

RESULTS AND DISCUSSION

By microscopic investigation, (Fig. 1a, b), 2D GO nanosheets with surfaces of tens of micrometers and thicknesses that reach up to atomic layer of carbon can be observed. These can build 3D structures of tens of micrometers thickness (Fig. 1c). Details about structural characterization of GO used for this study for the preparation of PVC/GO composites, including XRD, Raman, FTIR, DLS and XPS measurements, were presented in an research article published by Cotet et al. [12].

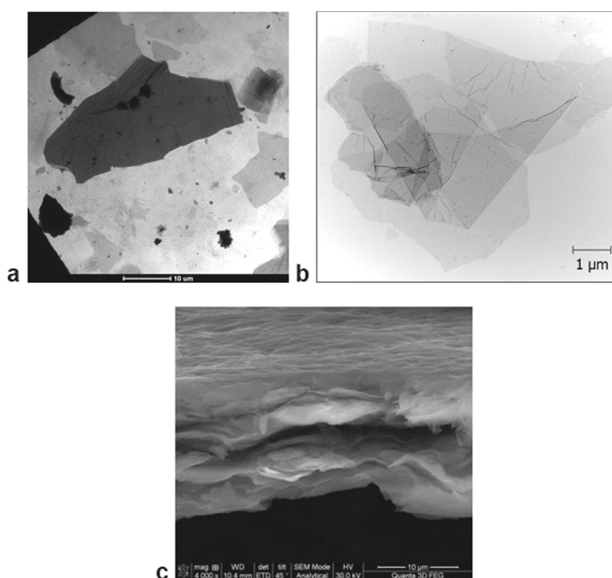


Figure 1. TEM (a), SPM (b) and (c) SEM micrographs for GO.

A selection of SEM images of PVC membranes is shown in Fig. 2. It is observed that in the case of PVC/GO composites with 3 and 5 wt.% GO, the membrane surface becomes rougher, in good agreement with the observations reported in Ref. [13] and confirmed by our studies. In this context, the surface properties of the samples have been analyzed by atomic force microscopy (AFM) using the WsxM5.0 software.

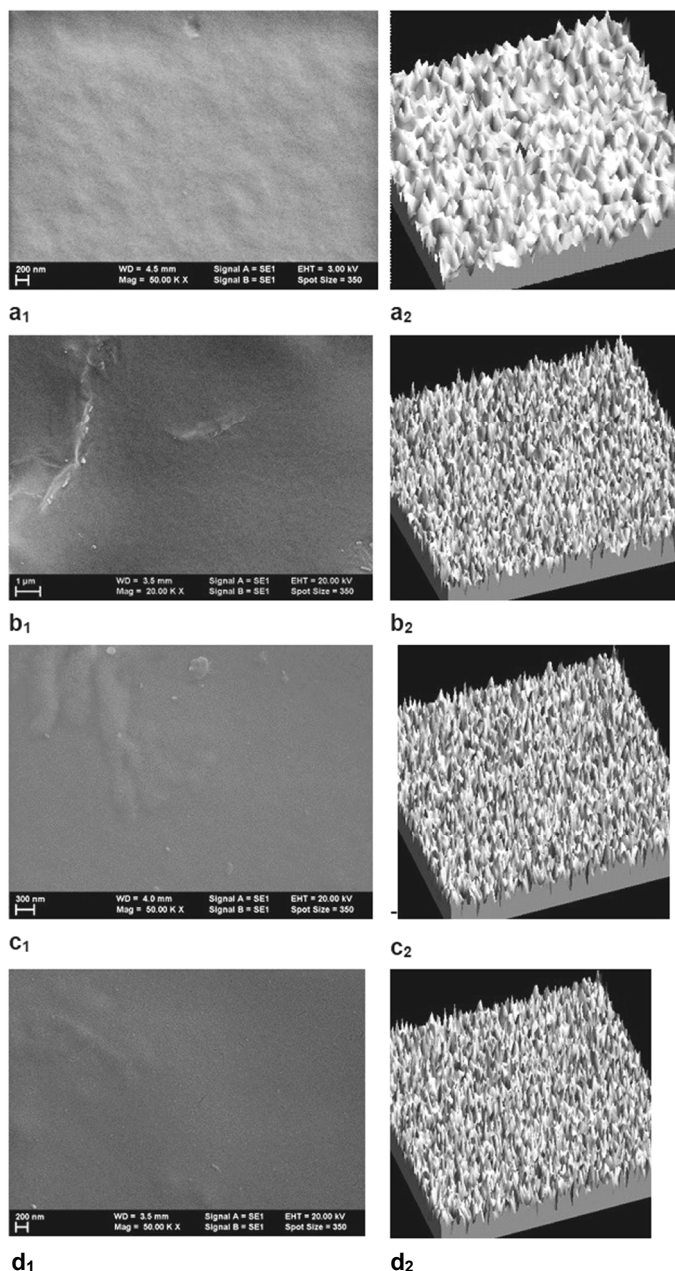


Figure 2. SEM images for the following membranes: PVC 0 wt.% GO (a₁), PVC 0.5 wt.% GO (b₁), PVC 3 wt.% GO (c₁), and PVC 5 wt.% GO (d₁). AFM images of the membranes: PVC 0 wt.% GO (a₂), PVC 0.5 wt.% GO (b₂), PVC 3 wt.% GO (c₂), and PVC 5 wt.% GO (d₂).

From AFM images the following values for roughness average and Root Mean Square (RMS) roughness are reported: i) 235 μm and 281 μm in the case of the PVC membrane; ii) 233 μm and 278 μm in the case of the PVC membrane having 0.5 wt.% GO; iii) 230 μm and 277 μm in the case of the PVC membrane having 3 wt.% GO and iv) 227 μm and 275 μm in the case of the PVC membrane having 5 wt.% GO.

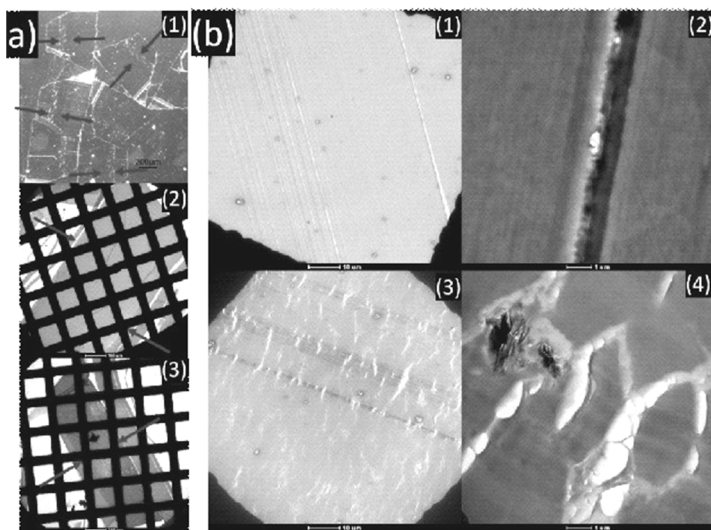


Figure 3. (a) Optical microscopy and TEM micrographs showing transversal cross-sections of (1) PVC 3 wt.% GO, (2) PVC 0 wt.% GO and (3) PVC 4 wt.% GO membranes with the membrane-resin boundary indicated with arrows. (b) Textural particularities induced by the presence and absence of GO filler as observed in the multi-scale TEM micrographs for (1-2) PVC 0 wt.% GO and (3-4) PVC 4 wt.% GO.

In order to gain a deeper understanding regarding the GO dispersion in the PVC matrix, a cross-sectional analysis was performed as presented in Fig. 3. Slices of the resin embedded membranes were investigated using optical microscopy and TEM. The cross-section of the PVC sample reveals a homogeneous aspect with some texture imperfections given by the irregularities of the glass blades used during sample sectioning. The sample containing GO indicates some additional features presented as microscale discontinuities, probably even more emphasized by the mechanical stress induced during the sample sectioning. Moreover, the observed irregularities found in the analyzed sections of the PVC 4 wt.% GO indicate a homogeneous distribution

at the microscale. At larger magnifications, morphological features specific to both individual and agglomerated graphene sheets are observed in the intimate vicinity of the irregularities. The results suggest that GO disperses throughout the entire volume of the membrane leading towards the formation of a nano-scale network. The parameters of the GO filler-based network (i.e. connectivity and percolation threshold) are considered to be strongly correlated with the synthesis parameters and filler concentration and to further influence the electric and thermal properties of the composite.

The FTIR spectra of the PVC samples and the PVC/GO composites are shown in Fig. 4.

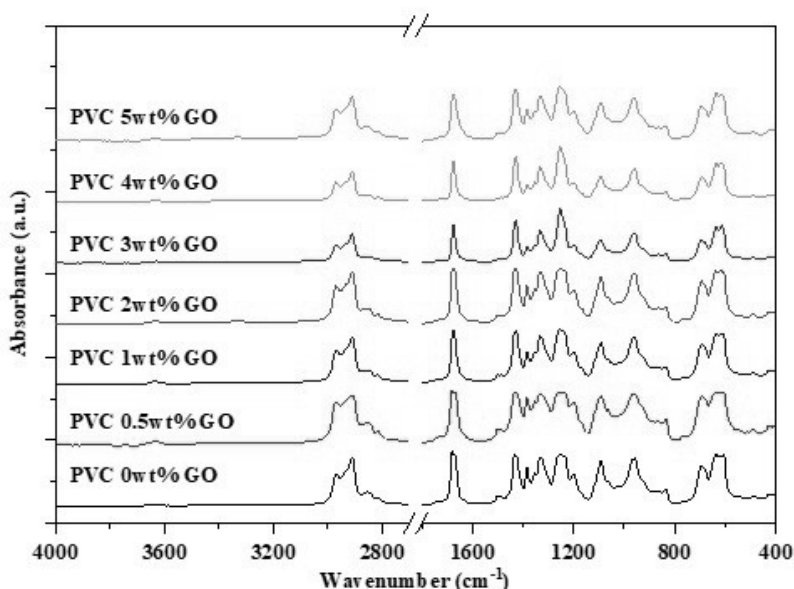


Figure 4. FTIR spectra of PVC and the following PVC/GO composites: PVC 0.5 wt.% GO, PVC 1 wt.% GO, PVC 2 wt.% GO, PVC 3 wt.% GO, PVC 4 wt.% GO and PVC 5 wt.% GO wt.%.

The absorption bands from 2981 cm^{-1} are attributed to the stretching vibration of the C-H bond, those from 2822 cm^{-1} to the asymmetrical stretching vibrations, and those from 1668 cm^{-1} to the stretching vibration of C=O, which are attributed to CO_2 from the background. At the absorption band at 1426 cm^{-1} , the deformation vibrations in plane of the CH groups can be identified, at 1340 cm^{-1} those of the deformation in plane of CH_2 , and at 1251 cm^{-1} the twisting vibrations of the CH. [14] At the same time, at 1091 cm^{-1} , the stretching

vibrations of the CH₂-Cl groups are observed, at 970 cm⁻¹ the rocking vibration of the CH in the cis position, at 695 cm⁻¹ the stretching vibration of the C-Cl, at 614 cm⁻¹ elongation vibrations of C-Cl and at 612 cm⁻¹ rocking vibrations of CH in trans position were identified. [14] The absorption bands related to PVC have been identified being consistent with the results found in related studies. Analyzing the spectra of the composites, the specific PVC bands, but no significant differences between the spectra can be observed and the presence of the characteristic bands for GO cannot be identified with certainty. Therefore, this analysis shows that FTIR spectroscopic technique is not sufficiently sensitive to highlight the presence of GO in the used concentration range.

In all diffractograms of the samples presented in Fig. 5 one large and two smaller, broad signals can be observed, suggesting the amorphous structure of the materials [14, 15]. In the case of pure PVC, these signals appear at 2θ ~18°, 24° and 40°, all characteristic for PVC according to previous literature. These amorphous reflections shift proportionally with the GO content, reaching ~ 20°, 26°, 42° in the case of PVC 4 wt.% GO. In the case of the PVC 5 wt.% GO sample there is no further shifting in the reflections, the diffractogram is dominated by an amorphous signal around 2θ ~ 25°.

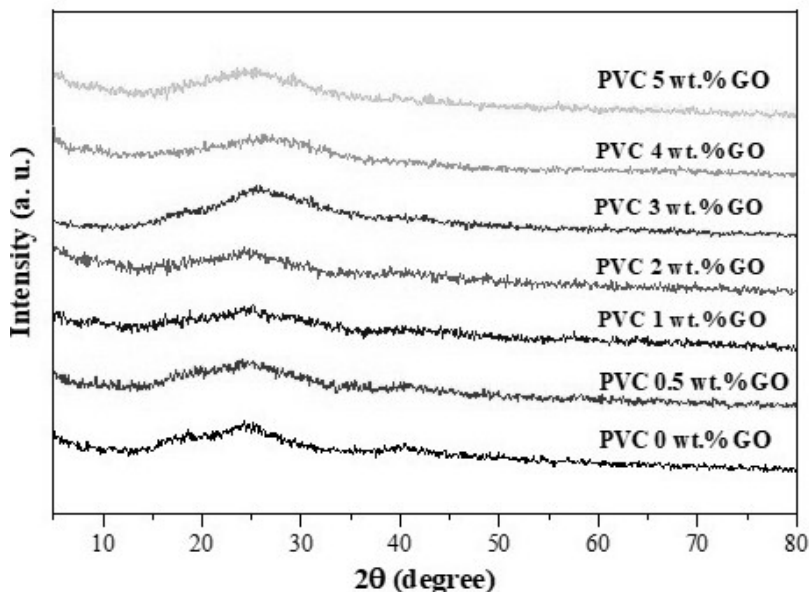


Figure 5. XRD results for pure PVC and the following PVC/GO composites: PVC 0.5 wt.% GO, PVC 1 wt.% GO, PVC 2 wt.% GO, PVC 3 wt.% GO, PVC 4 wt.% GO and PVC 5 wt.% GO.

These displacements may suggest the incorporation of GO into the polymeric matrix, that is altering the original structure of the PVC sample. The characteristic reflection of GO at $\sim 2\theta = 10^\circ$ cannot be clearly observed in any of the samples. [16] Apart from the shift of the above-mentioned reflections, no other significant differences were observed. This could mean that the amount of GO added in PVC/GO composites is too small to be detected by XRD measurements.

The Raman spectra of PVC and its GO composites recorded using the 514 nm excitation wavelength are shown in Fig. 6.

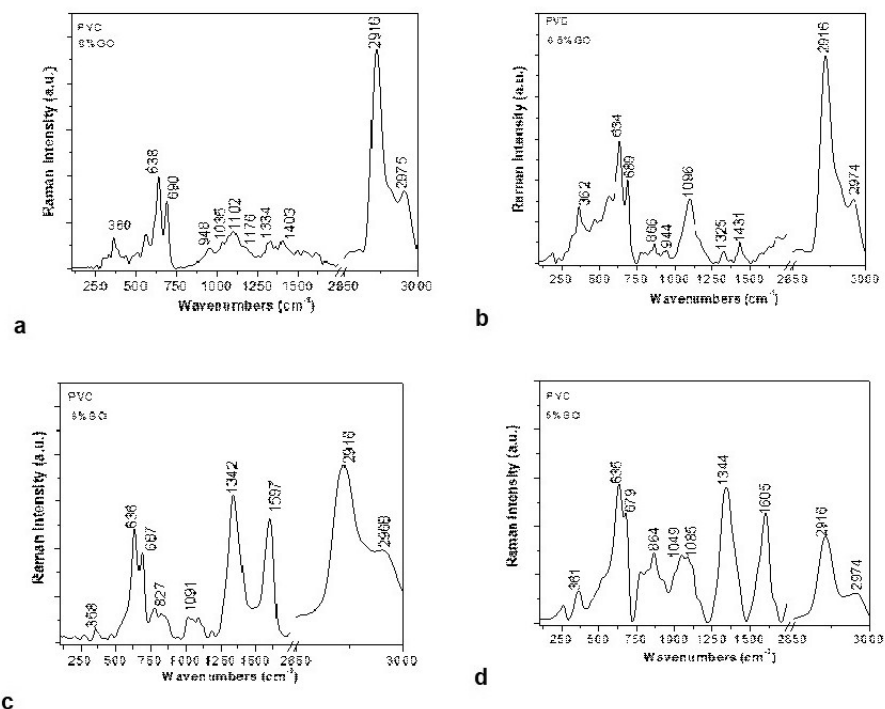


Figure 6. Raman spectra of the membranes: PVC 0 wt.% GO (a), PVC 0.5 wt.% GO (b), PVC 3 wt.% GO (c), and PVC 5 wt.% GO (d).

The main Raman lines of PVC are situated in the spectral ranges 300-500, 600-750, 950-1200, 1334, 1403-1430 and 2850-3000 cm⁻¹, being associated to the vibrational modes: C-Cl bond in the trans configuration of the polymer, C-Cl stretching [17, 18] C-C stretching, CH₂symmetrical stretching (2915-2920 cm⁻¹) and the CH₂ asymmetric stretching (2970 cm⁻¹) [19]. Figure 6a

highlights that the ratio between the relative intensities of the Raman lines in the spectral domains 600-650 and 2850-3000 cm^{-1} ($I_{600-650}/I_{2850-3000}$) has a value equal to 0.41. As increasing of GO concentration in the mass of the polymer, a modification of the $I_{600-650}/I_{2850-3000}$ ratio is observed. According to Fig. 6d in the case of PVC/GO composite with a 5 wt.% GO concentration, the $I_{600-650}/I_{2850-3000}$ ratio becomes equal to 1.63. The gradual decrease of the relative intensity of the Raman line of PVC from 2916 cm^{-1} in the presence of GO indicates the generation on the macromolecular chain of PVC of some structural units of the type Cl-CH=CH- and/or $-\text{CH=C-Cl-}$. The formation of such structural units indicates the partial dehydrogenation of the macromolecular compound which should result in the formation of new C-H and C-OH bonds on the GO surface. Formation of new C-H and C-OH bonds on the surface of the GO sheets originates in breaking C-O-C bonds from GO epoxy groups. In contrast with the GO sheets characterized by the I_D/I_G ratio equal to 0.9⁹, in the case of PVC/GO membrane composites having a GO concentration equal to 5 wt.%, the I_D/I_G ratio is equal to 1.23. This higher value of the I_D/I_G ratio indicates the formation of C-H bonds as a consequence of the conversion of carbon atoms with sp^2 hybridization (related to C=C bonds) to carbon atoms with sp^3 hybridization.

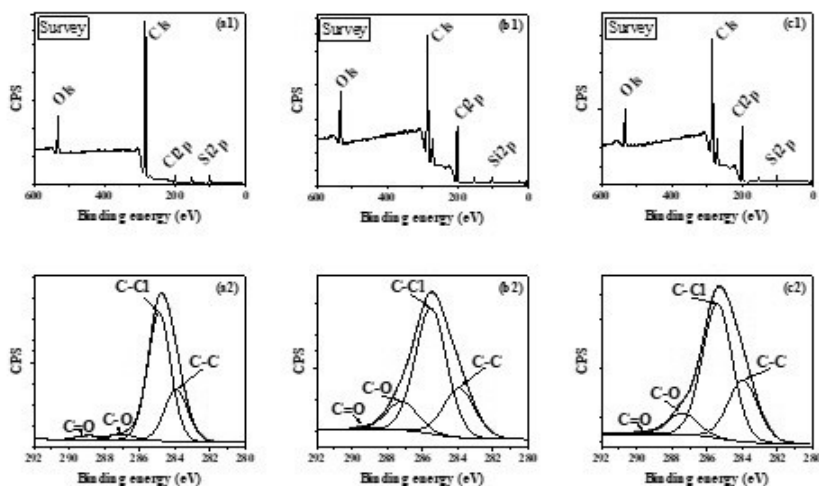


Figure 7. XPS spectrum selection, survey and C1s component (high resolution spectrum), for PVC (a1 and a2), PVC 0.5 wt.% GO (b1 and b2), PVC 5 wt.% GO (c1 and c2) samples.

The XPS spectra of the PVC/GO samples and a selection thereof are shown in Fig. 7 to highlight the influence of the presence of GO in the PVC/GO composite. Based on the literature, the C1s PVC line can be divided into two components, [20] at ~ 284 eV (C-C and C-H), ~ 285 eV (C-Cl). In addition to the C-C and C-Cl bonds, there are also the C-O bonds at 286.9 eV (2-3%) and C=O 288.5 eV (2-3%). With the addition of GO (PVC with 0.5 wt.% GO and PVC with 5 wt.% GO) the C1s peak is modified (Fig. 7b, c), suggesting that the synthesis was successful. In PVC with 0.5 wt.% GO, the C-O concentration is 13% and in PVC with 5 wt.% GO it is 10%. The analysis of the high-resolution spectrum of C1s shows that the concentration of C-C bonds increased with GO concentration suggesting that GO covers PVC (it is clearly the change of the C-C and C-Cl lines intensities ratio). The XPS measurements also show a decrease in chlorine concentration with increasing GO content.

CONCLUSIONS

This work reports about new results concerning the morphological and structural properties of the composites based on PVC and the GO sheets, obtained by mixing of two constituents when free membranes were resulted. The analysis of SEM and 3D images of the prepared PVC/GO membranes highlight a roughness for all six samples, with increasing the GO concentration in the PVC mass from 0 to 5 wt.%, the roughness average decreased from 235 to 227 μm . On the other hand, both SEM and TEM images proved that there are no agglomerations of the GO structures within the PVC/GO matrix contrast limit. XRD diffractograms revealed a down-shift of the main diffraction signal from 24° to 26° when the of GO concentration increases in the PVC/GO composite mass from 0 to 5 wt.%, the fact that certified the incorporation of GO in the polymeric matrix and the modification of the original PVC sample structure. In the FTIR spectra no significant difference is observed between the samples, but there are differences in the Raman lines and the XPS spectra. However, the Raman spectra analysis revealed that as increasing the GO concentration in the polymer mass, the ratio between the relative intensities of the Raman lines situated in the spectral ranges 600-650 and 2850-3000 cm^{-1} ($I_{600-650}/I_{2850-3000}$) increases as a consequence of the change of the GO carbon atoms hybridization from sp^2 to sp^3 . The analysis of the high-resolution XPS spectrum of C1s further showed an increase in the number of C-C bonds, the appearance of O-C=O bonds and the decrease of the chlorine concentration as the GO concentration increased.

EXPERIMENTAL SECTION

Materials

Natural graphite (Fluka; purum powder, <0.1 mm) powder (GF), H₂SO₄ 85% (SC Nordic Invest SRL, Cluj-Napoca), H₃PO₄ 85% (Merck), KMnO₄ (Merck, 99%), H₂O₂ 3% solution (SC "Hippocrates 2000" SRL, București), HCl 37% (SC Nordic Invest SRL, Cluj-Napoca), absolute ethanol (SC Nordic Invest SRL, Cluj-Napoca) were used for the synthesis of GO. Hydroxyethyl cellulose (HEC), lauryl peroxide (LPO), N,N'-dimethylformamide (DMF), poly(vinyl chloride) (PVC with Mw = 48.000, density = 1 g/mol at 25 °C) used for preparation of PVC membranes and composites were purchased from the Aldrich-Sigma company, these being used without further purification.

a) Synthesis of GO

The synthesis of GO was based on a three-step method. In the first step H₂SO₄ and H₃PO₄ (83 mL) were mixed in a 9/1 volume ratio [12, 21]. After 5 min. of mixing, 7.5 g of graphite was added at room temperature under stirring. The suspension was stirred for 10 min. and the as-prepared mixture was placed in an ice bath and after 20 min., 33 g of KMnO₄ was added gradually, maintaining the same stirring conditions. The mixture was removed from the ice bath after 2 h and kept under stirring at room temperature for 2 days. In the second step, the mixture was placed again in an ice bath and 550 mL of H₂O₂ was added gradually under stirring. After 1 h, the mixture was centrifuged (at 5000 rpm for 15 min.) and the supernatant was decanted. The remained solid material was then washed successively with 550 mL of H₂O (bidistilled), 275 mL of 37% HCl and 275 mL of absolute ethanol. The last two washes were repeated twice. During each wash, the solution was sonicated for 15 min. (using Bandelin Sonorex ultrasonic bath, model RK-510-H; P: 160/640W; f: 35 KHz) and centrifuged (at 5000 rpm for 15 min.). In the third step, the resulting solid was dispersed in 550 mL bidistilled water and sonicated for 15 min. A homogeneous dark brown suspension was obtained and kept in a sealed vessel for 5 days. Then, approximately 500 mL of this initial GO suspension was harvested by pipetting from the top of the vessel, poured and spread on a glass wafer and dried at room temperature. Mechanical exfoliation from the substrate was used to obtain a GO membrane (i.e. unsupported GO film). These membranes have been morpho-structurally characterized and used to obtain PVC/GO composites.

b) Preparation of the membranes of PVC and its composites with the GO sheets

To obtain the PVC membranes, 0.4 g PVC was dissolved in 10 mL THF and 10 mL DMF. The obtained solution was poured into a Petri dish and then deposited on a hob at 60 °C in order to evaporate the solvents. After one hour, the PVC membrane was dried under vacuum for another 6 hours until constant mass. In order to obtain PVC/GO composites, two solutions were prepared, the first containing 0.4 g PVC in 10 mL THF, and the second containing 1, 2, 4, 6, 8 and respectively 10 mg GO in 10 mL DMF. The two solutions were mixed and then the same procedure described for obtaining the PVC membranes was followed.

Characterization techniques

X-ray diffraction (XRD) was carried out on a Shimadzu XRD 6000 diffractometer using CuK α radiation ($\lambda=1.54$ Å), equipped with a graphite monochromator. The diffractograms were recorded in 2θ range from 10° to 80° with a speed of 2°/min.

IR absorption spectra were recorded with a FTIR Vertex 80 spectrometer, from Bruker, at room temperature, in the 400–4000 cm⁻¹ range, with a spectral resolution of 4 cm⁻¹, by using the well-known KBr pellet technique.

Raman spectra were recorded with a Raman spectrophotometer, T64000 model, from Horiba Jobin Yvon endowed with an Ar laser (the excitation wavelength being 514 nm). The Raman spectra were recorded with a spectral resolution of 1 cm⁻¹.

Transmission electron microscopy (TEM) investigations were performed on the GO flakes and polymer composites. The nanomaterial was dispersed in ethanol and deposited on the surface of carbon coated Cu grids. The composites were embedded in LR white resin and ultramicrotomed using glass blades. The slices were deposited on Cu grids for TEM investigations and on glass slides for optical microscopy studies. A FEI Tecnai G2 F20 X-Twin TEM operating at 200 kV was used in bright field mode. The SEM analysis were performed using a tabletop microscope Hitachi TM4000 plus (Hitachi High-Technologies, Japan), equipped with an energy-dispersive X-ray system (AZtec One EDS, Oxford Instruments Analytical Ltd., UK), at an accelerating voltage of 5 kV.

The SEM analysis of the GO flakes was performed using a tabletop microscope Hitachi TM4000 plus (Hitachi High-Technologies, Japan), equipped with an energy-dispersive X-ray system (AZtec One EDS, Oxford Instruments Analytical Ltd., UK), at an accelerating voltage of 5 kV.

SEM pictures of the PVC/GO composite membranes were recorded with Zeiss Gemini 500 scanning electron microscope. An analysis of the roughness parameters of these composites membranes was carried out using WSxM5.0 develop 9.3 software.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a PHI 5600ci Multi Technique system employing a monochromatic Al-K α source (1486.6 eV), a hemispherical analyzer and charge neutralization device. Samples were carefully fixed on a double-sided carbon tape to ensure that the sample particles covered the tape. Experiments were performed by operating the X-ray source with a power of 200 W, while the pressure in the analyzer chamber was in the range of 10⁻⁹-10⁻¹⁰ mbar. The binding energy scale was charge referenced to the C1s at 284.6 eV. Elemental composition was determined from survey spectra acquired at pass energy of 60 eV. High resolution spectra were obtained using analyzer pass energy of 20 eV. Analysis of the data was carried out with CasaXPS software. A Shirley background was used for all curve-fitting along with the Gaussian/Lorentzian product form (70% Gaussian and 30% Lorentzian).

The SPM data was processed with MountainsMap 7.4 software from Digital Surf as contact atomic force microscopy (AFM).

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REFERENCES

1. Z.M. Research; PVC Market (Rigid PVC And Flexible PVC) by Application (Pipes & Fittings, Wires & Cables, Films & Sheets, Bottles and Others) For Automotive, Electrical & Electronics, Construction, Packaging And Other End-User: Global Industry Perspective, Comprehensive <http://www.zionmarketresearch.com/report/pvc-market> (accessed Dec 18, 2019).
2. John Watson (Reports And Data); Polyvinyl Chloride (PVC) Market To Reach USD 88.02 Billion By 2027 <https://www.globenewswire.com/news-release/2020/02/13/1984885/0/en/Polyvinyl-Chloride-PVC-Market-To-Rreach-USD-88-02-Billion-By-2027-Reports-And-Data.html> (accessed Sep 18, 2020).

L. STINGESCU, C. CADAR, L.C. COTET, L. BAIA, K. SASZET, K. MAGYARI, A.G. MIHIS, C.I. FORT, M. STROE, E. MATEI, A. NILA, I. ANGHEL, M. BAIA, M. BAIBARAC, V. DANCIU

3. J. Hu; X. Jia; C. Li; Z. Ma; G. Zhang; W. Sheng; X. Zhang; Z. Wei; *J. Mater. Sci.*, **2014**, *49*, 2943–2951.
4. A. Godínez-García; D.D. Vallejo-Arenas; E. Salinas-Rodríguez; S. A. Gómez-Torres; J. C. Ruiz; *Appl. Surf. Sci.*, **2019**, *489*, 962–975.
5. F. Mindivan; M. Gökteş; *Polym. Bull.*, **2020**, *77*, 1929–1949.
6. H.J. Salavagione; G. Martínez; *Macromolecules*, **2011**, *44*, 2685–2692.
7. K. Deshmukh; G.M. Joshi; *Polym. Test.*, **2014**, *34*, 211–219.
8. S. Vadukumpully; J. Paul; N. Mahanta; S. Valiyaveetil; *Carbon N. Y.*, **2011**, *49*, 198–205.
9. K. Deshmukh; S.M. Khatake; G.M. Joshi; *J. Polym. Res.*, **2013**, *20*, 286, pp. 1-11.
10. V. Singh; D. Joung; L. Zhai; S. Das; S. I. Khondaker; S. Seal; *Prog. Mater. Sci.*, **2011**, *56*, 1178–1271.
11. S. Sava; C. Sarosi; B. Stanca; A. Tonea; C. Alb; D. Dudea; *Stud. Univ. Babeş-Bolyai Chem.*, **2015**, *60*, 71–80.
12. L.C. Cotet; K. Magyari; M. Todea; M. C. Dudescu; V. Danciu; L. Baia; *J. Mater. Chem. A*, **2017**, *5*, 2132–2142.
13. S.M. Hosseini; E. Jashni; M. Habibi; M. Nemati; B. Van der Bruggen; *J. Memb. Sci.*, **2017**, *541*, 641–652.
14. N. Ahmad; A. Kausar; B. Muhammad; *J. Plast. Film Sheeting*, **2016**, *32*, 419–448.
15. C. Niculăescu; L. Olar; R. Stefan; M. Todica; C.V. Pop; *Stud. Univ. Babeş-Bolyai Chem.*, **2018**, *63*, 63–70.
16. Y. Feng; C. He; Y. Wen; Y. Ye; X. Zhou; X. Xie; Y.W. Mai; *Compos. Part A Appl. Sci. Manuf.*, **2017**, *103*, 74–83.
17. K.A. Prokhorov; D.A. Aleksandrova; E.A. Sagitova; G.Y. Nikolaeva; T.V. Vlasova; P.P. Pashinin; C.A. Jones; S.J. Shilton; In *Journal of Physics: Conference Series*; 2016; p 012001.
18. F. Qiu; G. He; M. Hao; G. Zhang; *Materials (Basel)*, **2018**, *11*, 2139, pp. 1-15.
19. J.M. Hankett; C. Zhang; Z. Chen; *Langmuir*, **2012**, *28*, 4654–4662.
20. K. Artyushkova; J.E. Fulghum; *Surf. Interface Anal.*, **2001**, *31*, 352–361.
21. A. Pérez Del Pino; E. György; C. Cotet; L. Baia; C. Logofatu; *RSC Adv.*, **2016**, *6*, 50034–50042.