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Interfaces in biopolymer nanocomposites: Their role in the gas barrier properties and kinetics of residual solvent desorption



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<i>Keywords:</i> Biopolymers Cellulose nanocrystals Lauryl functionalization Interfaces Gas barrier film Solvent desorption	Poly(lactic acid) nanocomposite films were prepared by solvent casting method dispersing lauryl-functionalized cellulose nanocrystals in the biopolymer matrix. The gas transport properties of nanocomposites with different filler content were studied by gas phase permeation technique while the release of residual solvent molecules $(CHCl_3)$ was analyzed by Thermal Desorption Spectroscopy. The aim of this work is to study the correlations between the two processes that so far were studied separately. The analysis reveals that both the gas barrier properties of the nanocomposite and the kinetics of the residual solvent desorption are controlled by interface LNC-PLA layers. The improved gas barrier properties observed up to a critical filler content of 6.5 wt. % are attributed to the formation of a gas-impermeable PLA regions with thickness in the 10 nm order surrounding the functionalized filler particles. In the pure PLA matrix residual solvent molecules form small aggregates which desorb through a thermally activated process showing a peak at T = 393 K and following a zero-order kinetic

1. Introduction

Poly(lactic acid) (PLA) is a biopolymer exhibiting high tensile modulus (3 GPa), good mechanical strength (> 60 MPa), high workability showing compostable and recyclable nature [1]. Its monomer can be prepared from corn, sugar beet and biomass residues and the obtained polymer is decomposed by natural agents: is thus considered as carbon neutral polymer [2]. Its use in applications such as packaging and biomedical technologies requires physical-chemical modifications to overcome inherent drawbacks such as brittleness, poor thermal properties and high gas permeability [3]. The blending with other biopolymers [4], the addition of inorganic (nano-clay or montmorillonite), metal (Ag) and metal oxide (ZnO and CuO) nanoparticles and of bio-additives (plant extracts, ochitosan) are routes explored to improve the performance of this biopolymer in the application fields above mentioned [5].

Cellulose nanocrystals (CNs) are made of cellulose chains bound together with hydrogen bonds: CNs present rigid, elongate rod-shaped structures with diameter from few to 100 nm and length from tens to hundreds of nanometers. The high aspect ratio, large surface area (ca. $150 \text{ m}^2/\text{g}$), low density and biodegradability/biocompatibility of these nanostructures have stimulated interest toward their use as additive in

biopolymer nanocomposites [6].

process. In the nanocomposites, interface regions trap a fraction of residual solvent molecules that increases with the LNC content: solvent release occurs at higher temperatures and follows a first-order desorption kinetics.

In this communication, by reviewing results of our previous studies [7,8], we try to make a correlation between the gas transport properties of nanocomposite PLA films containing lauryl-functionalized $(CH_3(CH_2)_{10}CH_2)$ cellulose nanocrystals (LCNs) at different contents [7] and the thermally activated release of residual solvent molecules (chloroform, CHCl₃) [8]. The aim is to have a unified picture of the transport processes occurring in nanocomposite PLA films to face the problems occurring when application fields are considered.

A recent literature review on polymer nanocomposites for gas barrier applications remarks that: (i) significant decreases of the gas permeability by the addition of gas-impermeable fillers occurs using elongated or layered nanoparticles and (ii) filler contents larger than 20 vol. % are needed adding elongated nanoparticles while less than 10 vol. % is enough adding layered nanoparticles [9]. It is also reported that improvements of the gas barrier properties upon filler addition are attributable to two mechanisms. (i) The gas-impermeable filler particles that can act as physical obstacles for permeating molecules forcing them to follow tortuous pathways which are longer than the membrane geometrical thickness. This tortuosity effect was observed, for example, in polymer nanocomposites with dispersed spherical and layered silicate nanoparticles [10,11]. (ii) The modification of the gas transport

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properties of the polymer matrix due to the filler addition that reduces the polymer free volume [12] or increases of the polymer crystalline fraction [9]. Free volume reduction, was observed in polyurethane-silica nanocomposites [13] and in montmorillonite/styrene-butadiene rubber nanocomposites [14] while a decrease of the gas transport rates as consequence of an increased matrix crystallinity was observed in nanocomposites prepared using spherical silica nanoparticles [15,16], layered montmorillonite [17,18] and graphene oxide [19].

The novelty of the investigations here reported is the evidence that in this biopolymer nanocomposite an improvement of the gas barrier properties can be obtained adding elongated LNC nanoparticles at contents up to \sim 5 vol. %. Moreover, the micro-structure of only the polymer layers located at the filler-matrix interface is seen to affect the mechanism of gas transport. It is also revealed that the desorption kinetics of residual solvent molecules in the nanocomposite films is controlled by these polymer-filler interface layers.

Results of this investigation suggest that the control of the nanocomposite interface properties play an important role for applications in food and electronic packaging [20,21] and innovative medical material [22], but also in future technologies as, for example, laser propulsion where polymers act as matrix containing nanoparticles [23]. Ideas coming from this discussion could have basic importance because the role of residual solvent molecules in the control of different nanocomposite properties is not yet well investigated [24–26].

2. Experimental

Details regarding the preparation and functionalization of the cellulose nanocrystals, the preparation of nanocomposites and nanocomposite thin films as well as morphological, thermal and structural analysis have been reported in a previous paper [7]. Here we will recall, when necessary, specific morphological/structural information and report on the procedures utilized to carry out gas phase permeation measurements and Thermal Desorption Spectroscopy (TDS) analysis of residual solvent molecules (CHCl₃). For gas permeation and solvent desorption tests we used thin film samples with thickness $L \sim 50 \mu m$.

2.1. Gas transport test

We used CO₂, N₂ and D₂ as test gases and employed planar membranes shaped as discs with diameter $d=13.5 \pm 0.1 \text{ mm} > > L$. At time t = 0 one membrane side was exposed to the test gas kept at P_{feed} pressure; gas molecules permeate through the membrane to a continuously pumped Ultra High Vacuum (UHV) chamber at a rate $Q(t) = \frac{1}{4}\pi d^2 j_{exp}(t) = A j_{exp}(t)$ and here form a rarefied gas with partial pressure $P_{chamber}^{gas}(t)$. The permeation flux $j_{exp}(t)$ varies with time t as indicated by the relation $j_{exp}(t) = \frac{1}{A}RT_{chamber}^2 S_p P_{chamber}^{gas}(t)$ and can be thus monitored measuring $P_{dmamber}^{gas}(t \ge 0)$: in the previous relation $T_{chamber}$ is the temperature of the chamber wall. The equation:

$$j(t) = \frac{\Phi}{L} P_{feed} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n exp \frac{-Dn^2 \pi^2 t}{L^2} \right]$$
(1)

was used to fit $j_{exp}(t)$ curves and obtain the diffusivity *D* and permeability Φ of the examined test gas in the nanocomposites. See Refs. [27] and [28] for more detailed information.

2.2. Solvent desorption analysis

TDS experiments were carried out in a continuously pumped UHV chamber raising the nanocomposite temperature from T_0 = 300 K to T_f = 500 K with 0.12 K/s temperature ramp and monitoring by Quadrupole Mass Spectrometer (QMS) the ion currents signal $I_{m/e}$ pertinent to the m/e= 83, 85 and 47 CHCl₃ fragmentation products [29]. The $I_{m/e}$ signals provide a measure of the solvent desorption rate



Fig. 1. j_{exp} (t) curves obtained at T = 310 \pm 2 K and P_{HPS} = 40 kPa with CO₂. Solid symbols are experimental data pertinent to the reference PLA sample. Open symbols are experimental data pertinent to nanocomposite samples with different filler content. Each curve is labelled with the corresponding LNC content. Lines fitting the j_{exp} (t) data were obtained by Eq. (1).

 $j_{des}(t)$. See Ref. [8] for more detailed information.

3. Results and discussion

A complete report of the gas transport results is presented in Ref. [7]. As an example, in Fig. 1 we present the $j_{exp}(t)$ curves obtained with CO₂ at T = 310 ± 2 K and P_{feed} = 40 kPa: data pertinent to the pure PLA film are reported as solid symbols while data pertinent to nanocomposites films are reported as open symbols [7]. It is observed that the permeation flux decreases when the filler content increases up to the critical LNC concentration of 6.5 wt. %; then the flux increases adding further filler particles. At 10 wt. % filler content the CO₂ permeation flux in stationary transport conditions reaches a value comparable to that of pure PLA. The Dand Ø values, obtained fitting of the experimental $j_{exp}(t)$ curves, are reported in Fig. 2 as a function of the LNC content for the three test gases. The comparison of the D and Ø data reveals that, adding LNC filler particles, the gas permeability of all examined gases decreases up to the 6.5 wt. % critical content while the gas diffusivity D maintains a nearly constant value [7].

Structural analysis carried out by Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) on nanocomposite samples with filler content up to 15. wt. % did not reveal variations of PLA properties such as crystalline degree (2.2 \pm 0.4 wt. %), glass transition temperature (58 \pm 1 °C), melting temperature (166 \pm °C)



Fig. 2. Permeability (upper panel) and diffusivity (lower panel) values at $T = 310 \pm 1$ K of the examined PLA-LNC nanocomposites as a function of the LNC filler content. (triangles: D₂; squares : CO₂; circles : N₂).



Fig. 3. Cross section SEM micrographs of: pure PLA and PLA-LNC nanocomposites with different LNC contents. Fig. 3(e) shows a micrograph of cavity walls in the PLA + 6.5 wt. % LNC nanocomposite: arrows indicate dispersed LNC filler particles.

and decomposition temperatures (the decomposition process started at 270 °C and presented the maximum degradation rate at 365 °C) [7]. Thus we correlated the gas transport behavior in Fig. 2 with the filler dispersion state as revealed by the SEM micrographs reported in Fig. 3: adding filler particles, the gas permeability decreases as long as the LNC particles are well dispersed or form small clusters; their precipitation produces micrometric agglomerates and increases the gas permeability.

In the following we will focus our attention on the gas transport data pertinent to nanocomposites having filler content up the 6.5 wt. %. A simple estimate evidences that the gas permeability reduction cannot be attributed to the reduction of the PLA specific volume consequent to the addition of the LNC gas-impermeable filler. Nano-cellulose and PLA matrix have the following mass density values: $\rho_{NC}=1.50 \text{ g/cm}^3$ and $\rho_{PLA}=1.24 \text{ g/cm}^3$ and the relation $\varphi_{vol} = \frac{\rho_{NC}}{\rho_{PLA}} \varphi_{wt}$ holds between filler volume content φ_{vol} and weight content φ_{wt} [7]. In nanocomposites with 3 and 6.5 wt. % filler contents the filler volume contents are 2.5 and 5.4 %, respectively, but permeability data in Fig. 2 show a much larger permeability reduction.

To discuss the obtained results let us recall that the gas transport properties of a polymer matrix are influenced by the addition of gasimpermeable fillers by two mechanisms. Gas-impermeable filler particles force penetrant molecules to travel along effectively longer diffusive paths than in the pure matrix, depending on their content and aspect ratio: consequently the apparent penetrant diffusivity and thus permeability are reduced. Experimental diffusivity values reported in Fig. 2 exclude that this "tortuous path" mechanism as responsible of the improved gas barrier properties. Dispersed filler particles influence the physical-chemical properties of a polymer region of thickness l_{int} at the filler-matrix interface and can thus change the local value of the gas permeability, \mathcal{Q}_{int} . The permeability value of this polymer interface region is reduced with respect to that of the pure matrix if polymer chains well adhere to the filler particles (rigidified region); Øint is increased if the poor polymer-filler adhesion causes the formation open volume defects such as nano-cavities (void formation) [30,31]. Permeability data in Fig. 2 and SEM micrographs suggest that when the filler content is lower than 6.5 wt. % interfacial region surrounding dispersed filler particles are rigidified reasonably as a consequence of a local free volume reduction due to the interaction between the lauryl chains and the PLA macromolecular chains [7].

An estimate of the rigidified layer thickness can be obtained analyzing experimental transport data in the framework of literature permeation models of Mixed Matrix Membranes [27]. The dispersed filler particles (with permeability value \mathcal{O}_d) and the surrounding interface layers (with permeability value \mathcal{O}_{int}) are modelled as a dispersed "pseudo-phase" region of effective permeability \mathcal{O}_{eff} . The ratio between nanocomposite and matrix permeability, $\frac{\mathcal{O}_{NC}}{\mathcal{O}_{PLA}}$, can be then evaluated by the relation: $\frac{\mathcal{O}_{NC}}{\mathcal{O}_{PLA}} = \frac{2(1-\varphi) + (1+2\varphi)(\mathcal{O}_{eff} / \mathcal{O}_{PLA})}{(2+\varphi) + (1-\varphi)(\mathcal{O}_{eff} / \mathcal{O}_{PLA})}$ where φ is the volume fraction of the dispersed "pseudo-phase" in the nanocomposite [30].

Here we carry out an evaluation of the φ parameter looking at the geometry of the LNC particles as described by recently obtained TEM images in Fig. 4 (ThermoFisher Talos F200S, nanocellulose dispersed by ultrasonicator in acetone, a droplet of solution was let to evaporate on a TEM copper grid). TEM micrographs show that the preparation procedure described in Ref. [7] produced elongated LNC structures with 400 to 500 nm length and diameter $D = 2r_d \sim 20$ to 30 nm. The "pseudophase" particle can be thus described as a cylinder with length *h* and diameter $2r_d$ surrounded by a rigidified layer of thickness l_{int} . Because the relation $h > r_d$ holds, then $\varphi = \frac{(r_d + l_{int})^2}{r_d^2} \varphi_{vol}$ where φ_{vol} is the filler volume fraction in the nanocomposite.

Experimental data in Fig. 2 for filler content up to 6.5 wt% (that is ~ 5 vol. %) were reproduced assuming that the interfacial layer: (i) is nearly gas impermeable ($\emptyset_{int}/\emptyset_{PLA}$ 0) and (ii) has average thickness $l_{int} \cong 2r_d$ [7]. Data in Fig. 2 for larger filler contents were, on the contrary, explained as consequence of the formation of interface regions rich of open volume defects around the LNC precipitates [7]. It's thus possible to conclude that the polymer rigidification at the filler-matrix interface is responsible of the improved gas barrier properties. Such mechanism was also suggested in polymer nanocomposites prepared dispersing few layers of graphene nanoplatelets in low density polyethylene (LDPE) and in amine-modified epoxy resins films [32,33].

Considering nanocomposites with LNC content lower than 6.5 wt. % and their TDS spectra (see Ref. [8] for a wider data presentation and discussion), the normalized spectrum of the pure PLA film shows a narrow TDS peak at T_p = 393 ± 1 K with *FWHM* ~ 10 K. The peak onset at $T \cong 340 K$ shows an exponentially increasing edge and the peak finishes at $T \cong 400 K$ with a sudden cut-off: these features suggest that solvent release obeys to a zero-order kinetics. This spectrum is reproduced assuming that (i) desorption kinetics was controlled by the thermally activated release of solvent molecules from their trapping sites and (ii) the de-trapping rate parameter p was given by the Arrhenius relation $p(T) = p_0 e^{-\frac{Edes}{k_B T}}$ [8]; in the previous relation E_{des} is the



Fig. 4. TEM micrograph of LNC filler particle and corresponding electron diffraction pattern.



Fig. 5. CHCl₃ desorption spectra of the reference PLA sample (upper panel) and of the PLA-LNC nanocomposites (central and lower panels). In the figures open symbols are the experimental data (indeterminations are inside the size of the symbols). Dotted and dashed lines in the central and lower panels are fits of the TDS spectra obtained with the zero-order and first-order desorption kinetics (see text) while the solid line is their convolution. Fitting values of the E_{des}^0 and ε_D terms are reported in each panel.

molecule trapping energy and $p_0 = \frac{k_B T}{k} \simeq 1.0 \times 10^{13} \text{ s}^{-1}$ the molecule escape attempt frequency [34]. To fit the peak we used curves numerically obtained by the equation $j_s = -\frac{\partial \theta(t)}{\partial t} = p\theta(t)$ where $\theta(t)$ is the traps fractional occupancy. To reproduce the described features of this peak it was necessary to assume that the activation energy E_{des} was dependent on the trap fractional linearly occupancy: $E_{des}(\theta) = E_{des}^0 - \varepsilon_D \theta$ [8]. This Elovich-type functional form is often observed in desorption process of molecular species adsorbed on solid surfaces and the term ε_D accounts for attractive ($\varepsilon_D < 0$) or repulsive $(\varepsilon_D > 0)$ interactions between adsorbed molecules [35,36]. The fit of the TDS spectrum in the upper panel of Fig. 5 was obtained with $E_{des}^0 = 1.11$ eV and $\varepsilon_D = -0.08$ eV [8] indicating that residual solvent molecules attractively interact [37,38]. It is possible to conclude that the zero-order desorption kinetics was connected to the CHCl₃ release from small solvent aggregates dispersed in the PLA matrix. In fact the obtained ε_D value i) well compares with values found in the analysis of TDS spectra in different gas/surface systems showing zero-order desorption kinetics and ii) is comparable to the minimum of the Lennard-Jones potential energy curve between like molecules [39-43].

Interfacial PLA-LNC regions produces peculiarities in the TDS spectra of the nanocomposites. In fact, the spectrum of the nanocomposite with 3 wt. % LNC content presents a shoulder in the high temperature side of the desorption peak at T_{p} = 388 \pm 1 K while the

spectrum of the nanocomposite with 5 wt. % CNF content exhibits two partially overlapping narrow peaks at $T_{P,a}$ = 377 ± 1 K and $T_{P,b}$ = 400 ± 1 K. The nanocomposite TDS spectra were reproduced by the overlap of two peaks also obtained assuming the CHCl₃ de-trapping process as rate limiting step in the desorption kinetics [8]. These peaks are reported as dotted and dashed lines in the central and lower panels of Fig. 5. The narrow low temperature peaks were obtained assuming the same θ -dependent functional form for $E_{des}(\theta)$ as with the pure sample and using nearly same fitting parameters; the broader high temperature peaks resulted compatible with a first order kinetics process and were reproduced with $E_{des}(\theta) = E_{des}^0 = 1.21$ eV [8]. The first order desorption kinetics and the $\varepsilon_D = 0$ value indicated that this desorption channel does not involve aggregated CHCl₃ molecules [8]. The high temperature peak was thus attributed to the release of CHCl₃ molecules trapped in sites of the interface regions between PLA matrix and the surface-functionalized LNC filler particle, owing to the LNC gas impermeable nature [8]. The integrated area of this second peak, in fact, increases with the filler content and accounts for the release of \sim 46% and \sim 75% solvent molecules in the nanocomposite with 3 and 5 wt. % filler content, respectively [8]. Note that usual sites where gas molecules are trapped in polymer films are the polymer-substrate interface [44], specific moieties of the polymer chains [45] or microvoids [40].

4. Conclusions

The gas barrier properties of the nanocomposites consisting of a poly(lactic acid) matrix (PLA) containing nano-cellulose filler particles (NC) functionalized by grafting hydrophobic lauryl chain (LNC), are improved as long as filler particles are well dispersed in the PLA matrix: the enhancement of the gas barrier properties is attributed to the formation of rigidified PLA interfacial region with size l_{int} comparable to the LNC diameter. TDS spectra reveal that residual CHCl₃ solvent molecules are trapped in these interface regions and their release occurs at temperatures higher than those associated with the release of solvent molecules from small condensates dispersed in the PLA matrix. The present results suggest that PLA nanocomposites containing functionalized LNC particles are potential candidates for application in packaging and biomedical technologies when their preparation process ensures a high dispersion degree of the filler particles and the proper engineering of the internal interface layers.

CRediT authorship contribution statement

D. Rigotti: Resources, Writing - review & editing. **A. Pegoretti:** Writing - review & editing. **A. Miotello:** Writing - review & editing. **R. Checchetto:** Conceptualization, Methodology, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- D. Garlotta, A literature review of poly(lactic acid), J. Polym. Environ. 9 (2001) 63–84.
- [2] J.B. van Beilen, Y. Poirier, Production of renewable polymers from crop plants, Plant J. 54 (2008) 684–701.
- [3] L.T. Lim, R. Auras, M. Rubino, Processing technologies for poly(lactic acid), Prog. Polym. Sci. 33 (2008) 820–852.
- [4] Yu Long, Ruoyu Zhang, Junchen Huang, Jinggang Wang, Yanhua Jiang, Guohua Hu, Jian Yang, Jin Zhu, Tensile properties balanced and gas barrier improved poly(lactic acid) by blending with biobased poly(butylene 2,5-furan dicarboxylate), ACS Sustainable Chem. Eng. 5 (2017) 9244–9253.
 [5] H. Balakrishnan, A. Hassan, M. Imran, M.U. Wahit, Toughening of Polylactic Acid
- [5] H. Balakrishnan, A. Hassan, M. Imran, M.U. Wahit, Toughening of Polylactic Acid Nanocomposites: a Short Review, Polym. Plast. Technol. Eng. 51 (2012) 175–192.
- [6] G. Siqueira, J. Bras, A. Dufresne, Cellulosic bionanocomposites: a review of preparation, properties and applications, Polymers 2 (2010) 728.
- [7] D. Rigotti, R. Checchetto, S. Tarter, D. Caretti, M. Rizzuto, L. Fambri, A. Pegoretti, Polylactic acid-lauryl functionalized nanocellulose nanocomposites: Microstructural, thermo-mechanical and gas transport properties, Exp. Polym. Lett. 13 (2019) 858–876.
- [8] R. Checchetto, D. Rigotti, A. Pegoretti, A. Miotello, Chloroform desorption from poly(lactic acid) nanocomposites: a thermal desorption spectroscopy study, Pure Appl. Chem. (2019), https://doi.org/10.1515/pac-2018-1216.
- [9] C. Wolf, H. Angellier-Coussy, N. Gontard, F. Doghieri, V. Guillard, How the shape of fillers affects the barrier properties of polymer/non-porous particles nanocomposites: a review, J. Membrane Sci. 556 (2018) 393–418.
- [10] K. Mueller, E. Bugnicourt, M. Latorre, M. Jorda, Y. Echegoyen Sanz, J. Lagaron, O. Miesbauer, A. Bianchin, S. Hankin, U. Boelz, G. Perez, M. Jesdinszki, M. Linder, Z. Scheuerer, S. Castellò, M. Schmidt, Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields, Nanomaterials 7 (2017) 74.
- [11] Yanbin Cui, S.I. Kundalwal, S. Kumar, Gas barrier performance of graphene/ polymer nanocomposites, Carbon 98 (2016) 313–333.
- [12] G. Choudalakis, A.D. Gotsis, Free volume and mass transport in polymer nanocomposites, Curr. Opin. Colloid Interface Sci. 17 (2012) 132–140.
- [13] M. Sadeghi, M. Mehdi, B. Ghalei, M. Shafiei, Preparation, characterization and gas barrier properties of polycaprolactone based polyurethane-silica nanocomposite membranes, J. Membrane Sci. 427 (2013) 21–29.
- [14] Yi-Qing Wang, You-Ping Wu, Hui-Feng Zhang, Li-Qun Zhang, Bo Wang, Zhi-Feng Wang, Free volume of montmorillonite/styrene-butadiene rubber nanocomposites estimated by positron annihilation lifetime spectroscopy, Macromol. Rapid Commun. 25 (2004) 1973–1978.
- [15] V. Vladimirov, C. Betchev, A. Vassiliou, D. Bikiaris, Dynamic mechanical and morphological studies of isostatic polypropylene/fumed silica nanocomposites with enhanced gas barrier properties, Compos. Sci. Technol. 66 (2006) 2935–2944.
- [16] A. Vassiliou, D. Bikiaris, E. Pavlidou, Optimizing melt-processing conditions for the preparation of iPP/fumed silica nanocomposites: morphology, mechanical and gas permeability properties, Macromol. React. Eng. 1 (2007) 488–502.
- [17] M.D. Sanchez-Garcia, E. Gimenez, J.M. Lagaron, Morphology and barrier properties of nanobiocomposites of poly(3-hydroxybutyrate) and layered silicates, J. Appl. Polym. Sci. 108 (2008) 2787–2801.
- [18] H. Ghasemi, P.J. Carreaou, M.R. Kamal, S.H. Tabatarei, Properties of PET/Clay nanocomposite films, Polym. Eng. Sci. 52 (2012) 420–430.
- [19] H. Mahamood, A. Pegoretti, R.S. Brusa, R. Ceccatro, L. Penasa, S. Tarter, R. Checchetto, Molecular transport through 3-hydroxybutyrate co-3-hydroxyhexanoate biopolymer films with dispersed graphene oxide nanoparticles: gas

barrier, structural and mechanical properties, Polym. Testing (2019), https://doi.org/10.1016/j.polymertesting.2019.106181.

- [20] Y.H. Hwang, T. Matsui, T. Hanada, M. Shimoda, K. Matsumoto, Y. Osajima, Desorption behavior of sorbed flavor compounds from packaging films with ethanol solution, J. Agric. Food Chem. 48 (2000) 4310.
- [21] B. Muir, H.B. Duffy, M.C. Moran, Optimization of solvent desorption for chemical warfare agent and simulant compounds from poropack QTM using experimental design: methyl salycilate and di(propylene glycol) monomethyl ether, J. Chromatogr. A 1038 (2004) 183.
- S.C. Anand, J.F. Kennedy, M. Miraftab, S. Rajendran, Medical Textiles and Biomaterials for Healthcare, CRC Press, Boca Raton, 2006.
 J.H. Koo, M. Natali, J. Tate, E. Alicorn, Polymer nanocomposites as ablative ma-
- [23] J.H. Koo, M. Natali, J. Tate, E. Alicorn, Polymer nanocomposites as ablative material – a comprehensive review, Int. J. En. Mater. Chem. Prop. 12 (2013) 119–162.
- [24] N. Jouault, D. Zhao, S.K. Kumar, Role of casting solvent on nanoparticle dispersion in polymer nanocomposites, Macromolecules 47 (2014) 5246.
- [25] D.W. Janes, J.F. Moll, S.E. Harton, C.J. Durning, Dispersion morphology of poly (methyl acrylate)/silica nanocomposites, Macromolecules 44 (2011) 4920.
 [26] S.J. Meth, S.G. Zane, C. Chi, J.D. Londono, B.A. Wood, P. Cotts, M. Keating,
- [26] S.J. Meth, S.G. Zane, C. Chi, J.D. Londono, B.A. Wood, P. Cotts, M. Keating, W. Guise, S. Weigand, Development of filler structure in colloidal silica-polymer nanocomposites, Macromolecules 44 (2011) 8301.
- [27] D. Roilo, C.A. Maestri, M. Scarpa, P. Bettotti, W. Egger, T. Koschine, R.S. Brusa, R. Checchetto, Cellulose nanofibrils films: molecular diffusion through elongated nanocavities, J. Phys. Chem. C 121 (2017) 15437–15447.
- [28] R. Checchetto, P. Bettotti, R.S. Brusa, G. Carotenuto, W. Egger, G. Hugenschmidt, A. Miotello, Anomalous molecular infiltration in graphene laminates, Phys. Chem. Chem. Phys. 20 (2018) 24671–24680.
- [29] J.P. Johnson, L.G. Christophorou, J.G. Carter, Gas breakdown and high voltage insulating gases, J. Chem. Phys. 67 (1997) 2196.
- [30] M.A. Aaron, et al., Performance studies of mixed matrix membranes for gas separation: a review, Separat. Purificat. Technol. 75 (2010) 229–242.
- [31] R. Pal, Permeation models for mixed matrix membranes, J. Colloid. Interf. Sci. 317 (2008) 191–198.
- [32] D. Roilo, N. Patil, R.S. Brusa, A. Miotello, S. Aghion, R. Ferragut, R. Checchetto, Polymer rigidification in graphene- based nanocomposites: gas barrier effects and free volume reduction, Polymer 121 (2017) 17–25.
- [33] R. Checchetto, A. Miotello, L. Nicolais, G. Carotenuto, Gas transport through nanocomposite membrane composed by polyethylene with dispersed graphite nanoplatelets, J. Membrane Sci. 463 (2014) 196–204.
- [34] R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1996, p. 482.
- [35] A.M. Peers, Elovich adsorption kinetics and the heterogeneous surface, J. Catal. 4 (1965) 499.
- [36] J.W. Niemantverdriet, K. Markert, K. Wandelt, The compensation effect and the manifestation of lateral interaction in thermal desorption spectroscopy, Appl. Surf. Sci. 31 (1988) 211.
- [37] V.P. Zhdanov, Elementary Physicochemical Processes at Solid Surfaces, Springer, Science, New York, 1991, pp. 145–189.
- [38] K. Christmann, Surface Physical Chemistry, Steinkoppf, Darmstadt, 1991, p. 152.
 [39] M.H. Kloppfer, B. Flaconneche, Transport properties of gases in polymers: a bivliographic review, Oil and Gas Science Technol. 56 (2001) 223.
- [40] W.R. Vieth, K.J. Sladek, A model for diffusion in a glassy polymer, J. Colloid Sci. 20 (1965) 1014.
- [41] Kiyoshi Nagai, A simple rate equation useful for adsorption systems: analyses of thermal desorption spectra, Phys. Rev. Lett. 59 (1985) 2159.
- [42] S. Varma, P.A. Dowben, The effect of lateral interactions on thermal desorption of N₂ from Ni(100), J. Vac. Sci. Technol. A 8 (1990) 2605.
- [43] E.S. Hood, B.H. Toby, W.H. Weinberg, Precursor-mediated molecular chemisorption and thermal desorption: the interrelationships among energetic, kinetics and adsorbate lattice structure, Phys. Rev. Lett. 55 (1985) 2437.
- [44] J. Garcia-Turiel, B. Jerome, Solvent retention in polymer films studied by gas chromatography, Colloid Polym. Sci. 285 (2007) 1617–1623.
- [45] B. Ochiai, K. Yokota, A. Fujii, D. Nagai, T. Endo, Revbersible trap-release of CO2 by polymers bearing DBU and DBN moieties, Macromolecules 41 (2008) 1229–1236.