

Polydopamine Formation In Poly (Vinyl Alcohol) + Montmorillonite Blends Allows To Produce Flexible And Robust Materials.

Vincent BALL

Université de Strasbourg, Faculté de chirurgie Dentaire, 8 rue Sainte Elizabeth, 67000 Strasbourg, France.

Abstract: It is demonstrated herein that the spontaneous oxidation of dopamine by dissolved oxygen (at pH = 9.6) in blends of poly(vinyl alcohol) and montmorillonite clay allows to produce robust stable and flexible sheets of material upon solvent casting and drying. The size of the membrane is only limited by the surface area of the collector vessel. In the absence of dopamine, and hence polydopamine, the deposit obtained in the same conditions undergoes cracks and does not form a material with the desired shape. Some structural characterizations of the PDA@PVA-MMT membranes and of the PVA-MMT blends are undertaken.

I. INTRODUCTION

In the last 10 years polydopamine (PDA) films have been used to coat the surface of all classes of materials with a conformal coating starting from a solution of dopamine [1] or another catecholamine [2]. In the presence of an oxidant either dissolved oxygen or an exogenous oxidant [3] dopamine undergoes oxidation according to the Raper-Mason mechanism to yield 5,6-dihydroxyindole (DHI) [4]. DHI then undergoes oligomerization or polymerization to yield PDA precipitates in solution and homogenous films at all kinds of interfaces even at liquid/liquid and liquid/gas interfaces [5]. The choice of dopamine to conceive an universal adhesive layer was based on the fact that dopamine contains simultaneously an amine and a catechol moiety as L-Lysine and L-Dopa contain in the amino acid sequence of the *mefp* (*Mytilus edulis* foot proteins) proteins. These proteins are present at the byssal plaque of mussels and allow their strong adhesion to all kinds of materials in the presence of agitated water [6]. Whatever its nature, polymeric or that of a heterogeneous aggregate, PDA presents many structural and compositional analogies with eumelanin, the brown-black photoprotectant of the skin [7]. As eumelanin, PDA coatings interact with metallic cations and with proteins [8] allowing an extremely large set of applications in environmental and biomedical sciences [9].

Surprisingly, the use of PDA to design composite materials has been less considered than the functionalisation of materials with thin PDA coatings. It was found that when L-Dopa is oxidized in the presence of clays, the oxidation and self-assembly process of L-Dopa is not only accompanied by the formation of a black composite, in which the clays are exfoliated, but also by a decarboxylation of L-Dopa [10]. This finding was extended to other clays [11] and the oxidation of dopamine was used to modify the optical and mechanical properties of films made from the alternated deposition [12] of a polycation (poly(allylamine)) and Montmorillonite (MMT) [13]. It is also known that many adjuvants in the dopamine solution, like poly(vinyl alcohol) (PVA) modify the fate of the dopamine oxidation restricting the precipitation of huge aggregates and favouring the formation of stable, PVA containing, PDA particles [14]. It is the aim of the present article to investigate the possibility to obtain, in a one pot manner, a composite material containing both PDA, PVA and clays. Each component in this blend is expected to contribute to the properties of the composite. Namely, the clay (MMT) is expected to afford toughness to the obtained composite and PVA will contribute for its elasticity whereas PDA is expected not only to exfoliate MMT but also to provide some crosslinks through its well known adhesive properties [1, 2]. To check the influence of PDA, some control composites were prepared by blending PVA and MMT in the same proportion but omitting the oxidation of dopamine. It is shown that the PDA depleted composites crack upon drying whereas the PDA containing ones can be obtained in the form of large free standing, robust and hydrophilic sheets. In addition these sheets are anisotropic from an optical and wettability point of view and are stable when immersed in water.

II. MATERIALS AND METHODS

Chemicals and membrane preparation

Dopamine (ref. H8502), Montmorillonite (MMT, K-10 Lot 845602-518) and poly(vinyl alcohol) (PVA, ref. 341584) were purchased from Sigma-Aldrich and used without further purification. The molecular mass distribution of the used PVA lies between 89000 and 98000 g.mol⁻¹. PVA was dissolved at 50 mg.mL⁻¹ (5 % w/v) in hot water (60°C) and sonicated until an homogeneous solution was obtained. MMT was dissolved in water at pH = 10 (checked with a calibrated Hanna H22 pH meter) sonicated during half an hour in a water bath and then

agitated under magnetic stirring during 24 h. The MMT suspension was at 10 % w/v and was stable at least two days without significant sedimentation under these preparation conditions. MMT and PVA solutions were mixed volume by volume (10 mL of each) and the mixture was poured in a plastic Petri dish and allowed to dry at (25 ± 1) °C under a laminar flow hood. The same experiment was made but adding 40 mg of dopamine to the MMT and PVA mixture. This blend was agitated at 300 rpm during 16 h to allow for the formation of PDA. Before being poured in an identical Petri dish. The pH of the blend, about 9.6, was sufficient to allow for the auto-oxidation of dopamine (at an initial concentration of $2 \text{ mg}\cdot\text{mL}^{-1}$) by O_2 dissolved in water. The drying step in the laminar hood lasted over two days after which the mass of the Petri dish containing PVA-MMT (as a control) and PDA@PVA-MMT did not change any more implying the evaporation of all the weakly bound water. At that level the border of the PVA-MMT and PDA@PVA-MMT deposits were cut with a razor blade and the material was tried to be detached from the Petri dish with tweezers. Some experiments were also made omitting the presence of MMT, the concentration of all other reactants and the preparation conditions being held constant, to yield PDA@PVA composites.

Characterization of the obtained materials. The materials obtained in the Petri dishes as well as the materials detached from them were photographed with a digital camera. The thermal stability of the membranes was investigated by means of thermogravimetric analysis (Netzsch-STA 409 PC) in an air environment with a gas flow of $100 \text{ cm}^3\cdot\text{min}^{-1}$. 20 to 25 mg of precisely weighed material (either PDA@PVA, PDA@MMT or PDA@PVA-MMT) were deposited in open alumina crucibles. The temperature was increased at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from 25 to 800 °C. X-ray diffraction (XRD) experiments were performed with a Bruker DSC 500 diffractometer. The samples (un-exfoliated MMT alone, PVA-MMT, PDA@PVA and PDA@PVA-MMT) were glued on the sample holders and scanned in the reflection mode using $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) starting from an incidence angle of 3 °C with step sizes of 0.05° . Contact angle measurements were performed with a Kruss DSA25 contact angle goniometer by depositing water drops of 5 μL on both faces of the sheets detached from the Petri dish. The deposited drops were photographed with a digital camera and the contour line of the water/vapour interface was fitted to extract the average (left and right) contact angle. Five droplets were deposited on each material to get an average \pm one standard deviation.

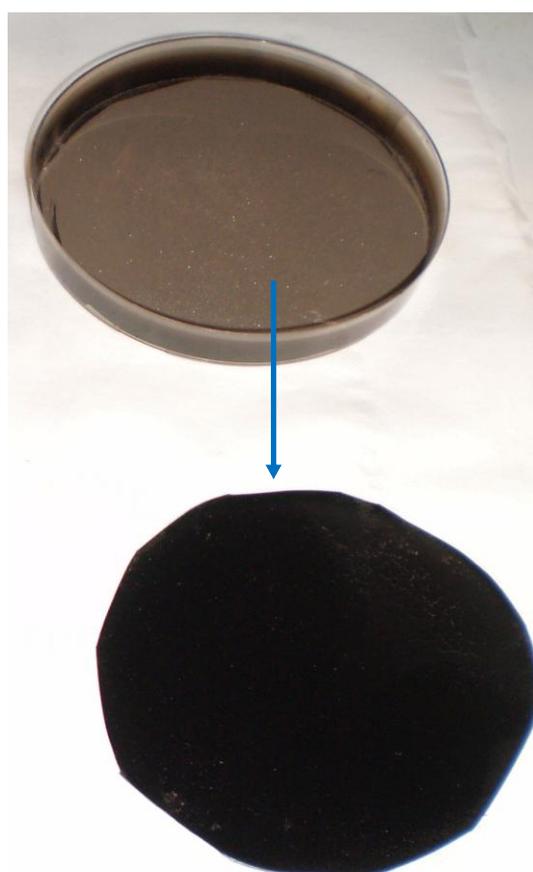
III. RESULTS AND DISCUSSIONS

The oxidation of dopamine at pH close to 9.6 produced a rapid change of the colour of the white PVA-MMT blend becoming brown-black after a few hours of agitation. Agitation was required to provide a continuous flow of oxidant, namely dissolved O_2 . After 16h, a duration normally sufficient to reach completion of dopamine oxidation, followed by its polymerization/self-assembly [1], the PDA@PVA-MMT mixture was poured in a plastic Petri dish 10 cm in diameter. This Petri dish was previously cleaned with ethanol and blown dry with a flow of filtered air. Some experiments were also performed with glass Petri dishes cleaned in the same manner, yielding to the same results as with the plastic Petri dishes. The mass of the filled Petri dishes was then measured and followed as a function of time during water evaporation under a laminar flow of air in a fume hood maintained at (25 ± 1) °C. After two days, no significant mass change (less than a mg in an hour) was recorded, meaning that all free and weakly bound water was evaporated. In the case of the PVA-MMT blend some cracks in the film were apparent and the resulting material was brittle. (Figure 1). It could be easily grinded in the form of a powder. On the other hand, in the case where PDA was formed in the presence of the PVA-MMT blend, the edge of the disk shaped black material was then cut with a razor blade to obtain an easily detachable sheet of material having the same lateral dimensions than the mold (ie the Petri dish) (Figure 2). The thickness of this sheet-like brown material could be easily changed by increasing the volume of PDA@PVA-MMT blend poured in the Petri dish. Some control experiments were also performed in which the clay was omitted in the preparation, the concentration of PVA and PDA being the same before the water evaporation process. In this case a black highly adhesive film was obtained at the bottom of the Petri dish. It was so highly adhesive to the mold that it could not be detached as a whole. Only small parts of it could be obtained and were used for characterisation purpose. Clearly the presence of MMT has some utility in the formation of the sheet-like material.

Concerning the PDA@PVA-MMT composite, it was also apparent that it is anisotropic in its optical shape: the part of the material exposed to air was bright whereas the face originally in contact with the Petri dish was dark (Figure 3). This is not intrinsically due to the presence of PDA in the composite because the small pieces of the PVA-MMT composite, in addition to many cracks, present also such a “dark” and “bright” appearance on their opposite faces. A closer look at the upper part of Figure 2 might provide an explanation for this change in glance. Indeed some material remains at the bottom of the mold upon detachment, meaning that the “dark” face of the obtained sheet reflects the internal structure of the material not its interface with the solid mold.



Figure 1: Picture of a PVA-MMT blend (10 mL of a 5 % w/v PVA solution and 10 mL of a 10 % w/v MMT suspension at pH = 10) after 2 days of drying.



Petri dish used for casting and drying

PDA@PVA-MMT membrane cut out from the Petri dish

Figure 2: Picture of a PDA@PVA-MMT blend (10 mL of a 5 % w/v PVA solution and 10 mL of a 10 % w/v MMT suspension at pH = 10) after 2 days of drying. PDA was formed in the PVA-MMT blend solution during 16 h under agitation at pH = 9.6. The upper part represents the Petri dish used as mold after detachment of the sheet like material (lower part).

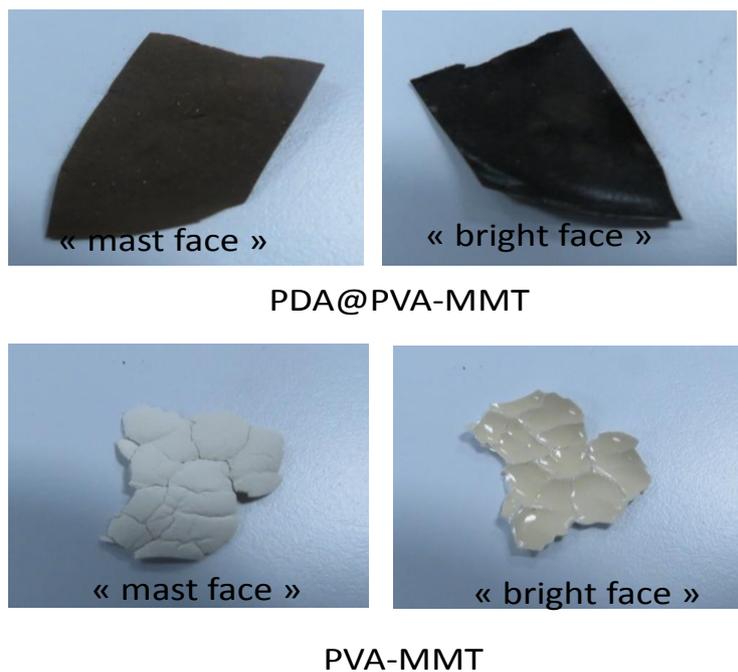


Figure 3: Mast and bright faces of the PDA@PVA-MMT sheets (cut with scissors from a larger piece of material) and of the crust like PVA-MMT composite.

It is now of interest to characterize some properties of the PDA@PVA-MMT sheets as well as of the “defective materials”, namely the PVA-MMT mixture and the PDA@PVA highly adhesive composite which could not be detached easily from the substrate. Thermogravimetric analysis reveals that the formation of PDA in the presence of PVA, in the PDA@PVA composite (not forming continuous sheets over the whole surface area of the mold) stabilises the composite. Indeed almost 12 % of the initial mass is still present at 800°C (Figure 4) whereas only about 3 % of the initial mass of PVA is still present at 800°C in the absence of PDA. Note that dopamine, and hence PDA, represents only 0.2 % of the solute mass in the blended solutions, because dopamine was solubilized at 2 mg.mL⁻¹. The PVA-MMT brittle composites undergo 3 thermally induced decomposition steps, described in Table 1, 56 % of the initial mass remaining at 800°C. Finally in the presence of PDA, the same decompositions steps but slightly shifted in temperature are found, and a 4th additional decomposition step is found (Table 1). The final residual mass amounts to 60 % for the PDA@PVA-MMT sheet (Figure 4). Again, the present PDA stabilizes the composite. It has to be noted that upon thermal degradation PDA undergoes a grafitization process yielding N doped graphite [15].

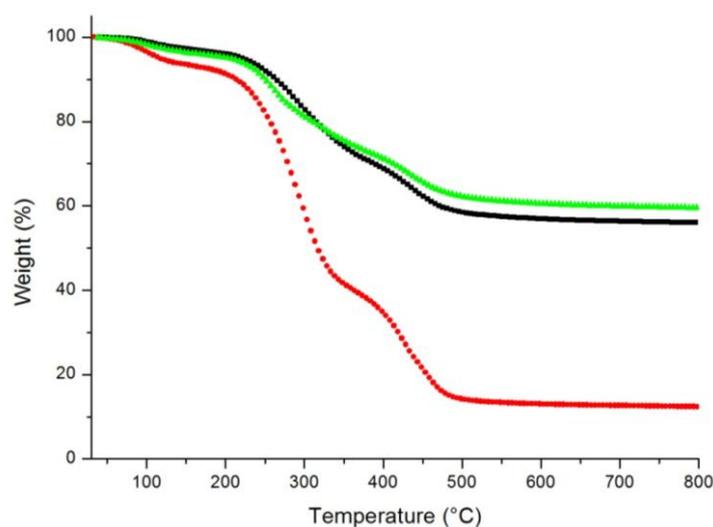


Figure 4: Thermogravimetric analysis of PVA-MMT (—), PDA@PVA-MMT (—) and PDA@PVA (—) composites.

	T_{max}^1 (°C)	T_{max}^2 (°C)	T_{max}^3 (°C)	T_{max}^4 (°C)	Residue at 800 °C (%)
PVA-MMT	110	287	434	-	56
PDA@PVA	102	296	423	-	12
PDA@PVA-MMT	96	257	319	435	60

Table 1: Results of the thermogravimetric analysis on the PVA-MMT, PDA@PVA and the PDA@PVA-MMT composites. T_{max} indicates the peak position of the corresponding decomposition step. Those temperatures have been obtained from differential TGA curves (data not shown)

In the case of the PVA-MMT and the PDA@PVA-MMT composites, the XRD curves show that the clays have been exfoliated and are randomly dispersed in the composites. There is no difference between the diffractograms taken with the bright and the mast face exposed directly to the X-ray beam (Figure 5). Surprisingly a broad peak is found in the case of the PDA@PVA composite, suggesting that PVA alone may change the self-assembly of PDA to create ordered domains of pretty small size. The broad peak at $2\theta \approx 19^\circ$ corresponds to a spacing of 4.7×10^{-10} m according to Bragg's law. This is higher than the 3.4×10^{-10} originating from graphitic structures which would correspond to a diffraction peak at $2\theta = 25.5^\circ$. Such graphitic domains are indeed present in PDA produced in the absence of any adjuvant [16]. Clearly PVA modifies, in a yet unknown manner, the self-assembly process of PDA. This finding is in agreement with data from the literature [14].

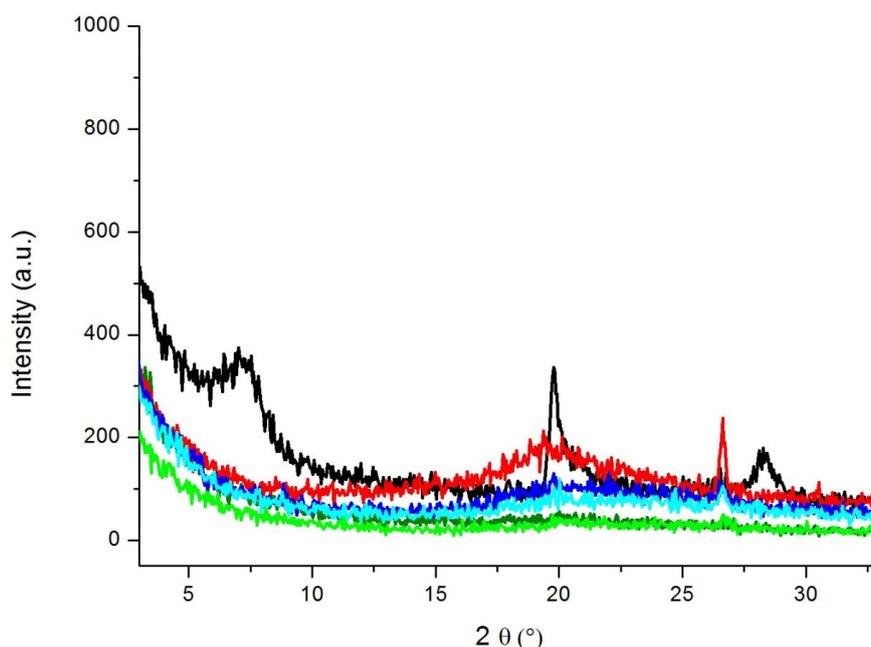


Figure 5: XRD scans of MMT (—), PVA-MMT bright face (—), PVA-MMT mast face (—), PDA@PVA (—), PDA@PVA-MMT bright face (—) and of PDA@PVA-MMT mast face (—).

Finally, we investigated the wettability of all the faces of the obtained materials, even if the PVA-MMT composite can only be obtained in the form of small pieces with plenty of cracks. It appears that the bright faces of the PVA-MMT composite (Figure 6) and of the PDA@PVA-MMT sheets are of comparable hydrophilicity (Table 2) with a static water contact angle of about 50° , significantly higher than the contact angle of the PDA@PVA composites (35°). Of major interest is that the apparent water contact angle measured on the mast faces of the PVA-MMT and the PDA@PVA-MMT composites are very close to zero. This most probably reflects the porous nature of the internal part of the composites. Indeed it was previously assumed that the anisotropic appearance of the PVA-MMT and of PDA@PVA-MMT composites stems from the detachment process exposing part of the internal structure of the composite to the air.

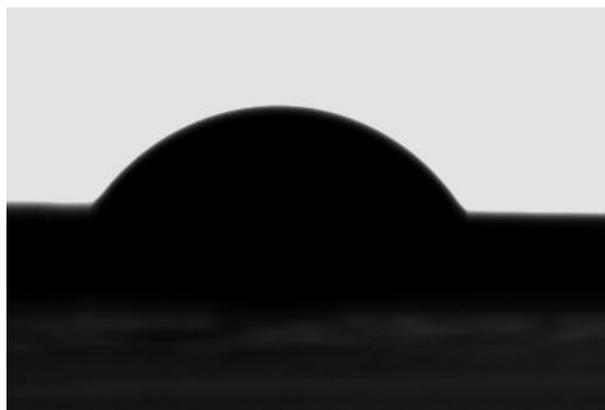


Figure 6: water droplet deposited on the bright face of a PDA@PVA-MMT composite and free standing membrane.

Samples	Static contact angle (water)
PDA@PVA	35 ± 1
PDA@PVA-MMT, bright face	50 ± 1
PDA@PVA-MMT, mast face	0
PVA – MMT, bright face	53 ± 1
PVA- MMT, mast face	0

Table 2: static water contact angles of the investigated composites.

This interesting finding of a different wettability behaviour on both faces of the useful PDA@PVA-MMT sheets may find interesting applications in terms of water purification. Namely since the mast face absorbs water, one may think to use the PDA present in the structure to retain heavy metal cations, a well-known property of eumelanin related materials [17]. From this perspective it has to be noted that the PDA@PVA-MMT composite remains stable when immersed in water for at least one day whereas the PDA free PVA-MMT composite slowly decomposes in a few hours. This observation again highlights the major contribution of PDA in stabilizing the obtained composites. It is anticipated, owing to its well described adhesive properties [1, 2] that upon its formation PDA provides some adhesive contacts between PVA chains and MMT platelets. Further characterisation in terms of the distribution and size of PDA in the PDA@PVA-MMT composite and in terms of their mechanical properties, using nanoindentation will be performed in future investigations.

IV. CONCLUSIONS

It is shown that stable sheets of PDA@PVA-MMT materials can be easily obtained by allowing for the oxygen triggered oxidation of dopamine (in alkaline conditions) in PVA-MMT blended solutions. However when PVA-MMT blends of identical composition are dried in a Petri dish mold, a brittle crack-full material which decomposes in water is obtained. This finding is attributed to the adhesive properties of PDA creating some non covalent bonds between PVA and the clay platelets. It has to be noted that the XRD data suggest that PDA has a different structure in the presence of PVA than in its absence. Of the highest interest is also the finding that the detachment of the PDA@PVA-MMT composite is easy, contrarily to the detachment of the highly adhesive PDA@PVA composite, and that the detachment process produces some anisotropy in the optical appearance as well as in the wettability of the obtained sheets of composite. These preliminary findings will be completed by other investigations aimed to characterize the distribution of PDA in the composite and its influence on the mechanical properties. The applications of these inexpensive and easy to prepare PDA@PVA-MMT materials will be investigated in terms of water purification.

ACKNOWLEDGEMENTS

Dr.KadirApaydin (CRP Henri Tudor, Luxembourg) is acknowledged for the XRD characterisations.

REFERENCES

- [1]. H. Lee, S.M. Delatorre, W.M. Miller, P.B. Messersmith, Mussel inspired surface chemistry for multifunctional coatings, *Science* 318, 2007, 426-430.
- [2]. S.M; Kang, J. Rho, I.S. Choi, P.B. Messersmith, H. Lee, Norepinephrine: Material- independent, multifunctional surface modification reagent. *J. Amer. Chem. Soc.* 131, 2009, 13224-13225.
- [3]. Q. Wei, F. Zhang, J. Li, B. Li, C. Zhao, Oxidant-induced Dopamine Polymerization for Multifunctional Coatings. *Polym. Chem.* 1, 2010, 1430-1433.

- [4]. M. D'Ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, Chemical and structural diversity in eumelanins: unexplored bio-optoelectronic materials, *Angew. Chem. Int. Ed.* 49, 2009, 3914-3921.
- [5]. F. Ponzio, V. Ball, Polydopamine at fluid interfaces. *Polym. Int.* 65, 22016, 1251-1257.
- [6]. B.P. Lee, P.B. Messersmith, J.N. Israelachvili, J.H. Waite, Mussel-inspired adhesives and coatings, *Ann. Rev. Mater. Res.* 41, 2011, 99-132.
- [7]. P. Meredith, T. Sarna, The physical and chemical properties of eumelanin, *Pig. Cell Res.* 19, 2006, 572-594.
- [8]. H. Lee, J. Rho, P.B. Messersmith, Facile conjugation of biomolecules onto surfaces via mussel adhesive protein inspired coatings, *Adv. Mater.* 21, 2009, 431-434.
- [9]. Y. Liu, K. Ai, L. Lu, Polydopamine and its derivative materials: synthesis and promising applications in energy, environmental, and biomedical fields, *Chem. Rev.* 114, 2014, 5067-5115.
- [10]. M. Jaber, J.-F. Lambert, A new nanocomposite: L-DOPA/laponite. *J. Phys. Chem. Lett.* 1, 2010 85-88.
- [11]. M. Jaber, M. Bouchoucha, L. Delmotte, C. Méthivier, J.-F. Lambert, Fate of L-DOPA in the presence of inorganic matrices: vectorization or composite material formation. *J. Phys. Chem. C* 115, 2011, 19216-19225.
- [12]. J.J. Richardson, J. Cui, M. Björnalm, J.A. Braunger, H. Ejima, F. Caruso, Innovation in Layer-by-Layer assembly. *Chem. Rev.* 2016, 116, 14828-14867.
- [13]. V. Ball, K. Apaydin, A. Laachachi, V. Toniazzo, D. Ruch, Changes in permeability and in mechanical properties of layer-by-layer films made from poly(allylamine) and montmorillonite postmodified upon reaction with dopamine. *Biointerphases* 2012, 7, art. 59.
- [14]. M. Arzillo, G. Mangiapia, A. Pezella, R.K. Heenan, A. Radulescu, L. Paduano, M.d'Ischia, Eumelanin buildup on the nanoscale: aggregate growth/assembly and visible absorption development in biomimetic 5,6-dihydroxyindole polymerization. *Biomacromolecules* 2012, 13, 2379-2390.
- [15]. R. Li; K. Parvez, F. Hinkel, X. Feng, K. Müllen, Bioinspired wafer-scale production of highly stretchable carbon films for transparent conductive electrodes. *Angew. Chem. Int. Ed.* 2013: 52, 5535-5538.
- [16]. C.-T. Chen, V. Ball, J de Almeida Gracio, M.K. Singh, V. Toniazzo, D. Ruch, M.J. Buehler, Self-assembly of tetramers of 5,6-dihydroxyindole explains the primary physical properties of eumelanin: experiment, simulation and design. *ACS Nano* 2013, 7, 1524-1532.
- [17]. L. Hong, J.D. Simon, Current understanding of the binding sites, capacity, affinity, and biological significance of metals in melanin. *J. Phys. Chem. B.* 2007, 111, 7938-7947.