

## Enhancing the thermo-oxidative stability of PLA through the use of hybrid organic–inorganic coatings

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**ABSTRACT:** PLA samples have been coated with organic–inorganic hybrid films containing SiO<sub>2</sub> as inorganic phase and two different types of organic phase PEO or PCL. Sol–gel solutions, spin coating deposition, and mild thermal treatments have been used to form thin protective coatings. Coated and uncoated PLA samples have been submitted to accelerated thermo-oxidative stresses at 120 °C in air up to about 400 h. The extent of the damage induced by this treatment has been evaluated by different techniques. Coated samples of both compositions are able to increase the resistance to thermo-oxidation of PLA as proved by the smaller reduction of molecular weight. This effect is probably deriving from the reduced oxygen permeability, as well as from the constrained outward diffusion and recombination of the cyclic oligomers produced by intramolecular transesterification reactions of polyester chains. Data so far collected underline also a long-term stability and adherence of the hybrid coatings during the entire aging process and hint at the possibility of using PLA in more demanding applications than that of packaging (i.e., electric industry, automotive field, or housewares). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43897.

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### INTRODUCTION

PLA is presently the most studied plastic material deriving from renewable sources. Although its main target of application, on account of the large amounts of consumed plastic and the short life-time of the products, is presently the packaging one, in the future other fields may be interested in using this bio-based plastic, that is, electrical industry as PBT or PET alternative or the automotive field to produce glass reinforced composites. Up to now, the main interests have been focused on the hydrolytic or biotic degradation of PLA, since these degradation conditions are mainly related to the post-use packaging degradation in the environment.<sup>1–6</sup> At a more limited extent, studies on thermal degradation (usually at temperatures near or above the melting point, to simulate transforming processes) have also been reported.<sup>7–11</sup> The thermal chain scission mechanism of PLA is quite complex because various reactions take place concurrently, influenced by the presence of “moisture, hydrolyzed monomers and oligomers, molecular weight, and residual metal-catalyst”.<sup>12,13</sup> It is usually accepted that the dominant pathway is the intramolecular and intermolecular ester exchange

which leads to the formation of lactide and cyclic oligomers<sup>10,12,14</sup> even though a chain-end scission (or unzipping mechanism) has been also observed.<sup>13</sup>

According to the results reported by Wachsen,<sup>14,15</sup> the thermal degradation of PLA is mainly due to an intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide with a simultaneous recombination of the cycling oligomers with linear polyesters through insertion reactions. The same authors observed that the kinetics of degradation can be modelled by a simple two-parameter model including a statistical degradation and a recombination reaction of macromolecules. This recombination step is particularly important in a closed system, where evaporation of low molecular weight cyclic molecules is hindered.<sup>15</sup>

When the effect of oxygen is also considered, the degradation process becomes even more complex. Södergård *et al.*<sup>9</sup> reported a slightly stabilizing effect of the oxygen in the first minutes of melt-processing, related to the deactivation of catalytic tin present in the PLA. Liu *et al.*<sup>11</sup> found, after a first step uninfluenced by the external environment, a remarkable decrease in the

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activation energy of the reaction when performed in air instead of nitrogen. Badia *et al.*<sup>16</sup> report that lower temperatures than those used in inert condition are necessary to start PLA degradation, when TGA experiments are performed in air.

Less attention has been devoted to the study of the mechanism of thermo-oxidation of PLA at lower temperatures (i.e., between the melting and the glass transition ones)<sup>7,17–19</sup> Gupta and Deshmukh found that the carbonyl carbon-oxygen linkage is the most likely one to be split by isothermal heating between 70 and 105 °C.<sup>7</sup> Rasselet *et al.*<sup>19</sup> analyzing the oxidation mechanism at temperature below 160 °C underlined a random chain scission mechanism, where oxygen plays a fundamental role, creating hydroperoxides and leading to the chain cleavage, according to the mechanism reported in Figure 1.

Organic–inorganic hybrid nanocomposites<sup>20</sup> derived from silicon alkoxyde by sol–gel process have been already recognized as protective and functional coatings on plastics to obtain high barrier properties for oxygen, water and low molecular weight additives,<sup>21,22</sup> flame and scratch resistance,<sup>23,24</sup> or antibacterial properties.<sup>25</sup> The sol–gel process has proved to be flexible enough for an efficient incorporation of organic oligomers or polymers, in particular for reactants bearing at least two reactive groups so that when they are involved in the hydrolysis–condensation reactions they can behave as flexible links between silica domains. Of course, the chemical nature of the organic component is of primary importance to obtain adhesion to the polymeric substrate that has to be protected.

Previous studies carried out on polyolefin substrates (low-density polyethylene and cross-linked polyethylene) had underlined how hybrid coatings of different compositions could significantly hinder the thermo-oxidative degradation, prolonging the service life of the materials.<sup>26,27</sup> This effect is attributable at the very low permeability of these materials compared with that of common polymers. For example, oxygen transmission rate (OTR) of 45- $\mu\text{m}$  thick LDPE films can be reduced more than three times when a 1- $\mu\text{m}$  thick hybrid coating is applied.<sup>28</sup>

In the present article, following those studies, the effect of hybrid organic–inorganic coatings on the thermo-oxidative resistance of PLA samples has been analyzed. Although our interest is to extend the use of PLA to nowadays uncommon applications, that need longer life times, also the packaging industry could indirectly benefit from the reduced oxygen permeability of the coated systems, prolonging aliments shelf-life, as already explored in literature.<sup>29,30</sup>

The inorganic phase selected for the coatings is made of silica deriving from the hydrolysis and condensation of tetraethoxysilane (TEOS), while polyethylene oxide (PEO) and polycaprolactone (PCL) alkoxy silane functionalized at the end chains with chemical groups able to react with the inorganic precursor forming an interpenetrating hybrid network, form the organic phase. The solubility of PEO in PLA is high as reported in literature,<sup>31</sup> while the miscibility of PCL in PLA is only partial but good adhesion between these two polymers has been often described.<sup>32,33</sup> Both polymers should thus have affinity to the substrate, providing an efficient adhesion to PLA as confirmed by the results reported by Iotti *et al.*<sup>29</sup>

The degradation of unprotected and coated PLA substrates has been investigated after accelerated tests in air at temperature slightly above the possible on-service one (120 °C) by evaluating the decrease in molecular weight through direct and indirect techniques.

## EXPERIMENTAL

### Materials and Coatings Preparation

Commercial PLA (Ingeo of NatureWorks Llc) was compression molded at 180 °C forming circular shaped disks (diameter 60 mm, 500  $\mu\text{m}$  thickness) and afterward annealed for 6 h in nitrogen at 120 °C.  $\alpha,\omega$  hydroxyl-terminated PEO ( $M_n \approx 2000$ ) and PCL ( $M_n \approx 2000$ ), high purity tetraethoxysilane (TEOS,  $\geq 99.0\%$ ), (3-isocyanatopropyl)triethoxysilane (ICPTES, 95%), and tetrahydrofuran (THF,  $\geq 99.0\%$ ) were supplied by Sigma-Aldrich (Milan, Italy) and used without further purification. Hydrochloric acid (37%, RPE) was purchased from Carlo Erba Reagents (Milan, Italy) and ethanol (EtOH,  $\geq 99.8\%$ ) by Fluka (Buchs, Switzerland).

PEO and PCL were triethoxysilane end-capped through bulk reaction with ICPTES according to the conditions described in details elsewhere.<sup>22,23,29</sup> As already described the progress of the reaction between hydroxy-terminated polymers and ICPTES was monitored using FT-IR spectroscopy while the expected structures of the final products were confirmed by the <sup>1</sup>H-NMR analysis.

Hybrids were prepared with a final organic–inorganic weight ratio of 30:70 following the procedure described in previous works.<sup>22,23,29</sup> The sol–gel solutions have been obtained according to the following procedure: triethoxysilane functionalized polymers thus obtained and TEOS were dissolved in tetrahydrofuran (usually at a concentration of about 30% w/v) until a homogeneous solution was obtained. Then EtOH, water, and hydrochloric acid were added to the solution at the following molar ratios with respect to ethoxide groups: EtO-/EtOH/H<sub>2</sub>O/HCl:1/1/1/0.05, where EtO- groups belong to both TEOS and triethoxysilane polymers. In all cases, the sol–gel solutions were heated in closed vials at 60 °C for 1 h under magnetic stirring, to promote partial hydrolysis–condensation of the reactants, before application to the polymer substrates.

After the above described thermal treatment, the sol–gel solutions have been used to coat, by two different steps, both sides of PLA disks by using a Laurell WS-400B-6NPP/LITE spin coater (Laurell Technologies Corporations, North Wales) operating at a spin rate of 1500 rpm for 30 s. After the first deposition, the coated disks were subjected to a thermal treatment at 60 °C for 2 h in an air-circulating oven before the deposition on the other side of the disks. At the end of depositions, all the coated and uncoated samples were subjected to a final thermal post-treatment at 80 °C for 24 h in an air-circulating oven. As derived by scanning electron microscopy the thicknesses of the coatings were  $1.6 \pm 0.2 \mu\text{m}$ . Hereafter uncoated samples will be labelled as PLA, while PLA substrate coated with coating hybrids having PEO or PCL as organic phase will be referred to as PLA-PEO and PLA-PCL, respectively.

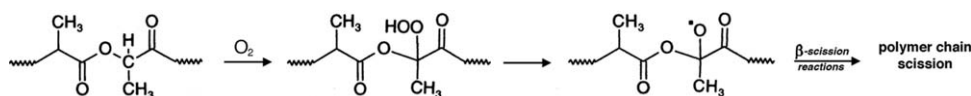


Figure 1. PLA oxidation and chain scission mechanism (ref. 19).

### Tests and Characterization

Coated and uncoated sample were aged, under ventilated conditions, at 120 °C in air up to 450 h. At scheduled times, samples were withdrawn after slow cooling to room temperature in a dry environment. Scanning Electron Microscopy (SEM) equipped with EDS analysis (Genesis 2000) were performed by a FEI XL20 instrument on coating surface, after gold/aluminium sputtering.

PLA substrates were submitted to differential scanning calorimetry (DSC) by means of a model Q10 (TA instruments) to investigate the amount of crystalline phase, as well as to disclose possible microstructural changes during the aging process. A first scan was performed at a heating rate of 10 °C/min up to 180 °C under a nitrogen flow rate of 60 mL/s, followed by a rapid quench (30 °C/min) to 15 °C, creating a fully amorphous sample. Afterward, a second heating scan at 10 °C/min was carried out up to 180 °C. From the first ramp the degree of crystallinity was obtained by integrating the melting peak and applying eq. (1):

$$X\% = \frac{\Delta H}{\Delta H^0} \times 100 \quad (1)$$

where  $\Delta H$  is the melting enthalpy of the substrate and  $\Delta H^0$  the melting enthalpy for the fully crystalline PLA, that is, 93.6 J/g.<sup>34</sup>

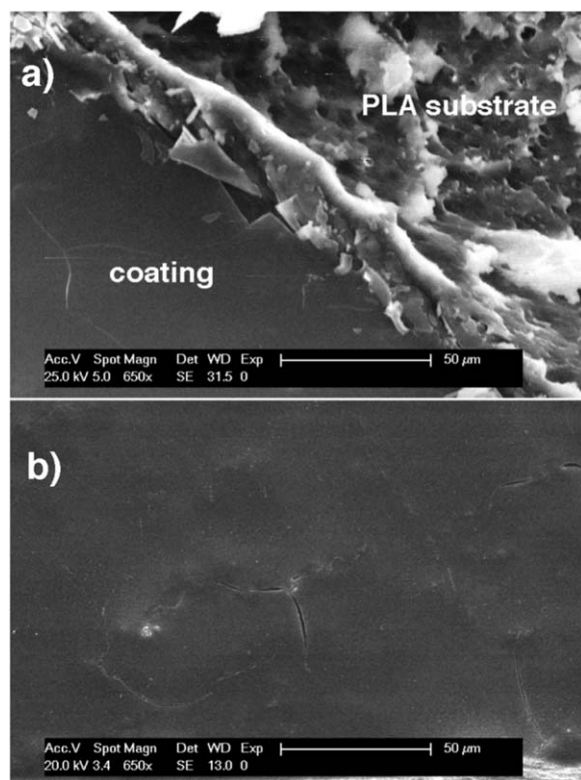


Figure 2. Coated surface before aging (a) and after 300 h at 120 °C (b).

From the second heating scan, the  $T_g$  was obtained as midpoint value according to ASTM E1356, as well as the enthalpy of crystallization by integrating the exothermic peak appearing at about 111 °C.

FT-IR spectra in ATR mode of aged and unaged PLA substrates, as well as the spectra of the hybrid covered substrates, have been reported in Supporting Information.

GPC analysis was used to investigate the molecular weight changes during the thermal degradation. A Waters system consisted of an isocratic pump (mod. 1515), a Refractive Index detector (Waters 2410), a UV/Vis detector (Waters 2487), and provided with a PLgel 5 µm MiniMIX-D column (250 × 4.6 mm) were used. The analysis was performed with chloroform as the eluent at a flow rate of 0.3 mL/min. Calibration was based on narrow polydispersity polystyrene standards (Polymer Laboratories, range 1250–340,000 g/mol).

### RESULTS AND DISCUSSION

The deposition of the sol-gel solutions by spin coating and the subsequent mild thermal treatments allow to obtain dense, homogeneous thin layers characterized by a good adhesion to the PLA substrate as already observed by other authors.<sup>29</sup> Figure 2 shows the morphology of a coating before the aging process (a) and after 300 h at 120 °C (b). In Figure 2(a) a scratch has been made on the sample surface before metallization with the aim to crack the coating applied on the substrate of PLA. It is important to notice that after the stress, Figure 2(b), the coating is still adherent to the PLA surface, almost continuous with only a few crevices appearing. EDS analysis (see Supporting Information) confirmed the presence of silica on the observed surfaces.

From the analysis of the DSC thermograms (reported in Supporting Information) some of the characteristics of the aged substrates have been determined. Figure 3 shows the amounts

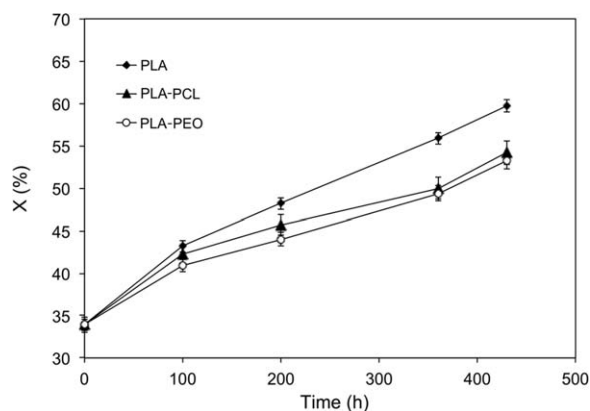
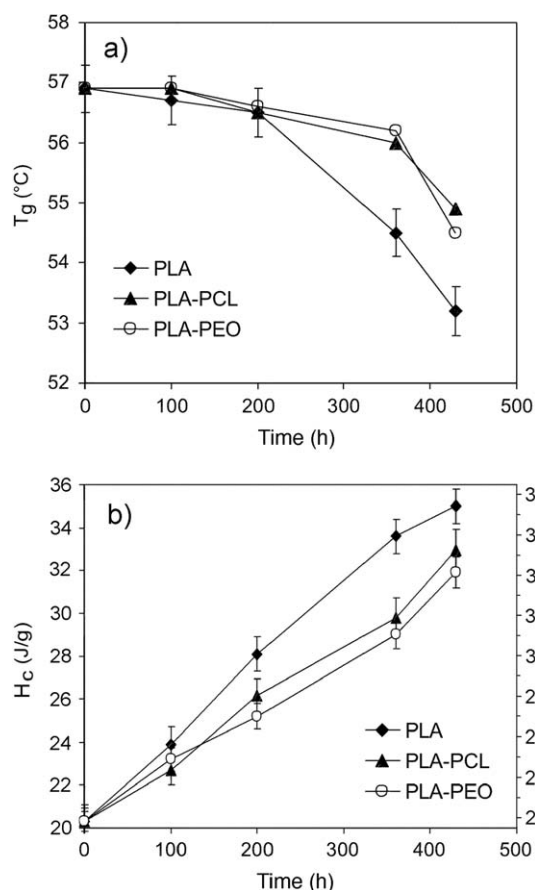
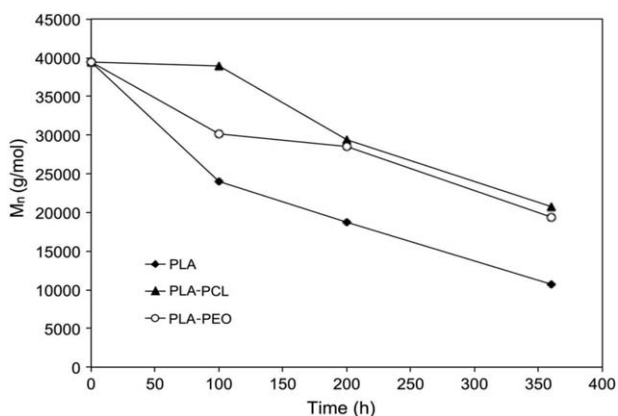


Figure 3. Amount of crystalline phase (first scan) as a function of aging.

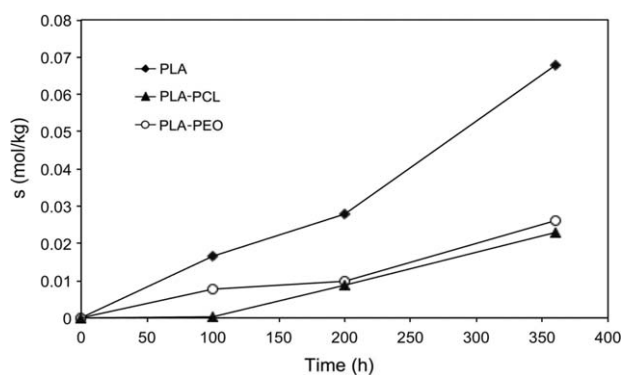


**Figure 4.** Second scan results: glass transition temperature (a) and crystallization heat (b) versus aging time.

of crystalline phase (%) determined from the first DSC scan. The increase of crystallinity during the thermo-oxidative test, outlined by amount of crystalline phase, derives both from the annealing process but also from the so called chemi-crystallization process caused by the polymer chains breaking in the amorphous phase.<sup>35</sup> This process can induce the partial erosion of the amorphous phase and the consequent formation of more mobile segments, able to be included in the existing crystals. This increase in crystallinity as degradation proceeds has been found in other polyesters submitted to hydrolysis.<sup>36</sup>



**Figure 5.** Number average molecular weight versus aging from GPC data.



**Figure 6.** Number of chain scissions versus aging time.

The glass transition temperature and the enthalpy of crystallization (as exothermic peak appearing at about 111 °C) have been determined from quenched samples in the second heating scan and the values are plotted in Figure 4(a,b), respectively. As can be seen, at all aging times, the uncoated sample shows a lower glass transition temperature and a higher enthalpy of crystallization than the coated samples. The difference is more evident as the aging time increases. As to what concerns the nature of the organic phase inside the coating (PEO or PCL), no significant differences are observed. To a first account, the slight decrease in glass transition temperature can be ascribed again to the decrease of molecular weight according to the Fox–Flory equation. Moreover, the increase in the crystallization enthalpy [Figure 4(b)] in the degraded samples is again deriving from the reduced length of the degraded polymeric chains. With the purpose to confirm this hypothesis the molecular weight distribution of various coated and uncoated samples was investigated through GPC analysis.

Figure 5 shows the change in the number average molecular weight ( $M_n$ ) derived from these experiments. The trends confirm the hypothesis derived from the DSC data on the larger decrease of molecular weight in the unprotected PLA versus PLA coated substrates. As for the previous results, the effect of the different organic phase in the hybrid coating is comparable.

Eventually, in Figure 6, the amount of chain scissions derived by applying eq. (2)<sup>37</sup>:

$$S(t) = \frac{1}{M_n(t)} - \frac{1}{M_n^0(t)} \quad (2)$$

where  $M_n^0$  is the average number molecular weight before degradation, and  $M_n(t)$  the value at time  $t$ , has been reported.

Data relative to the extent of chain scissions confirm the hypothesis previously made on the protective effect of the coatings, showing a number of chain breaks of about one-third in comparison with the uncoated PLA. In accordance with the proposed PLA chain degradation mechanism, the protective effect of the hybrid coatings is probably due to their lower oxygen permeability, able to reduce the reaction of oxygen with the radicals deriving from tertiary CH bond that is responsible of an alkoxy radical formation that can decompose by  $\beta$ -scission mechanism (Figure 1). A further contribution to the polymer stability is probably due to the constrained outward diffusion of volatile degradation products of PLA. In accordance with the thermal



degradation mechanism proposed by Wachsen *et al.*,<sup>15</sup> these low molecular weight products are mainly composed by lactide and cyclic oligomers able to recombine with linear polyesters through insertion reactions.

## CONCLUSIONS

Adherent and continuous organic–inorganic coatings have been deposited on the surfaces of untreated PLA substrates. The hybrid coatings remain coherent to the substrate even after a strong and prolonged thermal stress, showing only a limited amount of cracks. No substantial differences have been found between the performance of the two polymers, PEO and PCL, used to formulate the organic phase in the coatings. The extent of damage induced by thermo-oxidation can be reduced as demonstrated by the limited decrease (investigated by direct and indirect techniques) of molecular weight in protected PLA substrates when compared with uncoated ones. This effect is probably due to the barrier property of the coatings toward oxygen able to promote the radical chain scission, and toward the outward diffusion of the cyclic oligomers produced by intramolecular transesterification reactions that promotes their recombination with linear polyesters through insertion reactions. These results suggest longer service life and the possibility to extend the application fields of this material.

## REFERENCES

1. Li, S. M.; McCarthy, S. *Biomaterials* **1999**, *20*, 35.
2. Gorrasi, G.; Pantani, R. *Polym. Degrad. Stabil.* **2013**, *98*, 1006.
3. Karamanlioglu, M.; Robson, G. D. *Polym. Degrad. Stabil.* **2013**, *98*, 2063.
4. Kim, M. N.; Park, S. T. *J. Appl. Polym. Sci.* **2010**, *117*, 67.
5. Cerkez, I.; Worley, S.; Broughton, R.; Huang, T. *Polymer* **2013**, *54*, 536.
6. Gonzalez, M.; Ruseckaite, R.; Cuadrado, T. *J. Appl. Polym. Sci.* **1999**, *71*, 1223.
7. Gupta, M.; Deshmukh, V. *Colloid Polym. Sci.* **1982**, *260*, 514.
8. Carrasco, F.; Pagès, P.; Gámez-Pérez, J.; Santana, O.; Maspoch, M. L. *Polym. Degrad. Stabil.* **2010**, *95*, 116.
9. Södergård, A.; Näsman, J. *Polym. Degrad. Stabil.* **1994**, *46*, 25.
10. Kopinke, F. D.; Remmler, M.; Mackenzie, K.; Möder, M.; Wachsen, O. *Polym. Degrad. Stabil.* **1996**, *53*, 329.
11. Liu, X.; Zou, Y.; Li, W.; Cao, G.; Chen, W. *Polym. Degrad. Stabil.* **2006**, *91*, 3259.
12. McNeill, I.; Leiper, H. *Polym. Degrad. Stabil.* **1985**, *11*, 309.
13. Fan, Y.; Nishida, H.; Shirai, Y.; Tokiwa, Y.; Endo, T. *Polym. Degrad. Stabil.* **2004**, *86*, 197.
14. Wachsen, O.; Reichert, K.; Krüger, R.; Much, H.; Schulz, G. *Polym. Degrad. Stabil.* **1997**, *55*, 225.
15. Wachsen, O.; Platkowski, K.; Reichert, K. H. *Polym. Degrad. Stabil.* **1997**, *57*, 87.
16. Badia, J. D.; Santonja-Blasco, L.; Martínez-Felipe, A.; Ribes-Greus, A. *Bioresour. Technol.* **2012**, *114*, 622.
17. Badia, J.; Strömberg, E.; Ribes-Greus, A.; Karlsson, S. *Eur. Polym. J.* **2011**, *47*, 1416.
18. Pluta, M.; Murariu, M.; Alexandre, M.; Galeski, A.; Dubois, P. *Polym. Degrad. Stabil.* **2008**, *93*, 925.
19. Rasselet, D.; Ruellan, A.; Guinault, A.; Miquelard-Garnier, G.; Sollogoub, C.; Fayolle, B. *Eur. Polym. J.* **2014**, *50*, 109.
20. Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. *J. Mater. Chem.* **2005**, *15*, 3559.
21. Amberg-Schwab, S.; Katschorek, H.; Weber, U.; Hoffmann, M.; Burger, A. *J. Sol-Gel Sci. Technol.* **2000**, *19*, 125.
22. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Pasquali, L.; Nannarone, S. *Polymer* **2004**, *45*, 805.
23. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S.; Pasquali, L.; Nannarone, S. *Polymer* **2003**, *44*, 4463.
24. Amerio, E.; Fabbri, P.; Malucelli, G.; Messori, M.; Sangermano, M.; Taurino, R. *Prog. Org. Coat.* **2008**, *62*, 129.
25. Marini, M.; De Niederhausern, S.; Iseppi, R.; Bondi, M.; Sabia, C.; Toselli, M.; Pilati, F. *Biomacromolecules* **2007**, *8*, 1246.
26. Saccani, A.; Toselli, M.; Pilati, F. *Polym. Degrad. Stabil.* **2011**, *96*, 212.
27. Saccani, A.; Toselli, M.; Pilati, F.; Fabiani, D.; Palmieri, F. *Polym. Degrad. Stabil.* **2011**, *96*, 2080.
28. Toselli, M.; Pilati, F.; Marini, M.; Doghieri, F.; De Angelis, M.; Minelli, M. *Eur. Polym. J.* **2008**, *44*, 3256.
29. Iotti, M.; Fabbri, P.; Messori, M.; Pilati, F.; Fava, P. *J. Polym. Environ.* **2009**, *17*, 10.
30. Bang, G.; Kim, S. W. *J. Indus. Eng. Chem.* **2012**, *18*, 1063.
31. Sheth, M.; Kumar, R. A.; Davé, V.; Gross, R. A.; McCarthy, S. P. *J. Appl. Polym. Sci.* **1997**, *66*, 1495.
32. López-Rodríguez, N.; López-Arraiza, A.; Meaurio, E.; Sarasua, J. R. *Polym. Eng. Sci.* **2006**, *46*, 1299.
33. Simoes, C.; Viana, J.; Cunha, A. *J. Appl. Polym. Sci.* **2009**, *112*, 345.
34. Fischer, E.; Sterzel, H. J.; Wegner, G. *Colloid Polym. Sci.* **1973**, *251*, 980.
35. Fayolle, B.; Verdu, J. *Eur. Polym. J.* **2011**, *47*, 2145.
36. Muthuraj, R.; Misra, M.; Mohanty, A. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42189.
37. Saito, O. *J. Phys. Soc. Jpn.* **1958**, *13*, 1451.