PHOTOCHEMICAL APPROACH AS A STRATEGY TO RECYCLE RICE HUSK LIGNIN AND POST-CONSUMER POLYSTYRENE

Daniele G. Müller (1), Maria C. S. Bulhosa (1), Evelyn C. do C. Schenque (1), Marcelo P. da Rosa (1), Jessica S. da Silva (1), Paulo H. Beck (1) and Felipe Kessler (1)

(1) Photochemistry and Materials Chemistry Research Group. School of Chemistry and Food. Federal University of Rio Grande (FURG), Brazil

https://doi.org/10.21452/bccm4.2018.10.08

Abstract

The complete use of biomass and also the efficient management of waste materials are big challenges that must be overcome in this century. The work presented in this article uses lignin extracted from rice husk, using the organosolv method, as a filler in the residual expanded polystyrene (PS) matrix to obtain a PS/lignin composite. Two different carboxylic diacids (adipic acid and itaconic acid) were also employed as aditives. The initial materials and solvent were mixed and exposed to a medium pressure UV radiation source. The concentration of the lignin content was varied to evaluate its effect on the final material. The material was characterised using UV-Vis, FTIR, EDS, MEV, GPC, and mechanical assays. The spectroscopic and chromatographic data showed that 10 min of exposure was enough to promote changes in the polymeric chain. Due to the new spectroscopic features, a photo-grafting reaction occurred resulting in a stable PS/Lignin composite. Morphological analysis showed that even with a magnification of 40,000X some conditions result in films with great homogeneity. The mechanical tests showed a reduction in the tensile strength value with an increased lignin content, but in general, maintained the value of Young's modulus. Photochemical reactions were performed using a low complexity setup, in fast and mild reaction conditions, generating new uniform materials from polymeric residue and industrial waste.

1. INTRODUCTION

The increasing technological development of our society is leading to a serious imbalance between the environmental, economic, industrial, and social areas. Waste management has developed at different speeds throughout the world. Some parts of the world only recently in the past few decades, changed from waste being left in the streets to being treated and recycled using several methods and techniques and creating a very profitable industry. In the particular case of polymeric materials, some problems generated by the post-consumer polymers can be cited: i) the continuous increase in the amount of waste generated outstrips the collection, recycling, and disposal capacities; and ii) synthetic polymers take a long time to degrade, needing management of the disposal sites for centuries.

General specifications have been developed, trying to achieve controlled degradation, like resins based on natural polymers[1], biopolymers[2], green polymers[3] .However, increasing oil production and the low cost of synthetic polymers make green material alternatives less attractive to industry. Natural polymers, especially those originating from biomass, are an interesting source for new materials. The renewable characteristic and the possibility to develop products free from carbon emissions agrees with the principles of green chemistry. Emerging countries produce large amounts of biomass due to their commodity-based economies. Rice husk is an example of an undervalued biomass resource generated by the food industry. On average the rice husk composes 22% of the grain[4]. The main components of the rice husk are polysaccharides (cellulose and hemicellulose), lignin and silicates, in proportions that vary slightly, depending on the plant and the soil that it grows in[5]. Lignin is a potential source of new materials due to its phenylpropanoids units. This random polymer is the second most abundant polymer in nature, present in almost all plant life. The chemical diversity, abundance, and its huge potential have motivated several studies to identify applications like polymeric precursors[6], a carbon source for nanomaterials[7], blends and composites[8].

Photochemical methods are mainly based on photo-induced chemical processes. Chemical reactions can be induced if molecular groups show efficient reactivity once exposed to a light source. Depending on the chemical properties, specific reaction mechanisms can be achieved. Common chemical reactions like eliminations, additions, and dimerization in general, can induce the crosslink of macromolecule chains during UV exposure.[9] In addition, UV-assisted treatments usually have a simple experimental setup and low cost, being suitable for several industrial processes. Photochemical grafting has being used with success in composites, nanocomposites, biosensors[10]. Using a post-consumer PS and lignin extract from rice husk, the objective of this work was to synthesise Lignin/PS composite via the photochemical route. The results show that in a simple, fast, and low-cost synthesis route it is possible to obtain new polymeric materials, combining the strength of lignin and PS its versatility.

2. EXPERIMENTAL SECTION

2.1 Materials

Lignin extracted from rice husk using the organosolv method following the procedure of Rosa et al.[11] and was used as a macromolecule to be grafted. Expanded PS from discarded protective packaging was used without a purification process. Ethyl acetate (≥ 99%), hexane dioic acid (adipic acid), pureness ≥99%, and 2-methylidenebutanedioic acid (itaconic acid), pureness 99%, were purchased from Sigma-Aldrich, were used as received.

2.2 Synthesis of composites

All materials were synthesised using 1.0 g of PS, varying the lignin concentration in 2, 5, 10, 20 and 50% (w/w). 150 mL of ethyl acetate was added. Adipic acid (0.005 g) or itaconic acid (0.002 g) were used as the reaction controller. The system (PS–LO-dicarboxylic acid-solvent) was stirring at room temperature for 30 min. After this, the system was exposed to UV radiation using a medium pressure mercury lamp (400W) for 10 min, under magnetic stirring at room temperature. After the reaction, the polymer solution was poured into a petri dish and allowed to evaporate at ambient temperature and pressure. All materials were named by the carboxylic acid used (AA or IA) followed by the percentage of LO (2, 5, 10, 20, and 50).

2.3 Analysis and characterization.

All precursors and products were characterised using spectroscopic analysis in the UV/visible region (UV-Vis) Infrared Fourier Transform Spectroscopy (FTIR-ATR) analysis were performed using a Shimadzu spectrophotometer - IR PRESTIGE 21. Gel Permeation Chromatography (GPC) were used to determinate the molecular weights of all samples (model Viscotek, VE 2001) equipped with one column (PS-DVB) and triple detector (refractive index, viscosimetric, and by light scattering). For the mechanical tests, five samples analysis were performed at room temperature, following the ASTM-D-88215 standard. The sample thickness was measured using a Mitutoyo micrometre (0.001 mm 0-25mm), and the cross-sectional area was calculated by the average of ten measurements. The maximum stress and the maximum elongation distance were measured by a texturometer, model TA XT plus, manufactured by Stable Micro Systems(UK). The Young’s modulus was calculated by the relation between the initial distance and the distance at the break. Scanning Electron Microscopy (SEM) generated images, using a JEOL JSM-6610LV electronic microscope (Japan). Composition and semi-quantitative analysis of each element were performed by Energy Dispersive Spectroscopy (EDS) technique. Samples of each composite were analysed using a JEOL JSM-6610LV electronic microscope (Japan) using 15 KeV acceleration energy.

3. RESULTS AND DISCUSSIONS

The UV-Vis spectra of all samples (data not shown) present typical bands originating from pristine PS like the π–π* transition of the C=C in the aromatic rings at 250-275nm.[12] It is also noted that this region matches with the lignin UV-Vis spectrum in that the majority have substituted aromatic rings and oxygenated groups in its structure, responsible for the π–π* and n–π* transitions. Oxygenated groups bonded to aromatic rings can increase the width of this band (220-280 nm), which allows lignin in natural environment to protect the plant from UV radiation.[13] After the reaction the structure of spectra changed.

FTIR-ATR analysis is presented in Figure 1, in both figure it is possible to compare the pristine PS spectrum with LO/PS composite with a load of 5% and 50%. When the pristine PS spectrum is compared with AA5 and AA50 samples spectra, the typical bands and peaks of PS remain, however, after the reaction some changes also are visible: symmetric and asymmetric aliphatic C-H stretch peaks have shifted from 2924cm^{-1} and 2852 cm^{-1} (PS), respectively, to 2922 cm^{-1} and 2848 cm^{-1} (AA5 and AA50). This shift is related to electron acceptor groups bonded to the main chain of PS.[8] A significant C-H stretch shift occurs for AI samples (Figure 1) indicating that the polymer chain changes more for samples with AI than AA. All composites show a wide C=O stretch band (~1718cm^{-1}) and seems to increase intensity when the lignin content increases. LO used in this study is rich in hydroxyl and carbonyl groups which we believe it was the main molecular group involved in the grafting onto some of the PS chain. It is important to observe the absence of hydroxyl peaks (3100-3600 cm^{-1}). The strong C-O-C stretch peaks present in all samples at 1265 cm^{-1} (Figure 1) indicate that a grafting reaction occurred. In this spectrum region also was identified C-O bending peaks at 1328 and 1217 cm^{-1} which are typical signals for syringyl and guaiacyl lignin groups.[14].

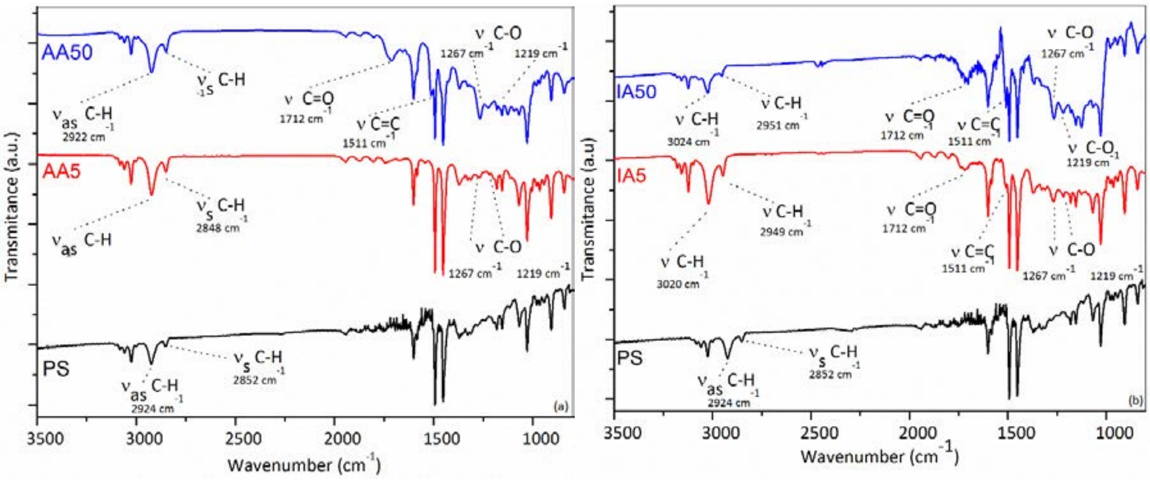

Figure 1. FTIR spectra for: (a) pristine PS (PS) and composites LO/PS prepared with adipic acid with 5% of lignin (AA5) and 50% of lignin (AA50); (b) pristine PS (PS) and composites LO/PS prepared with itaconic acid, with 5% of lignin (IA5) and 50% of lignin (IA50).

The UV-Vis data has revealed that after the photochemical reaction, the electronic transitions has suffered dramatical changes, showing new bands, yet maintaining the PS typical UV-Vis spectrum bands. The changes observed in FTIR-ATR spectra confirm the presence of lignin in the analysed samples and also some interesting features like the shift of aliphatic C-H peaks. Hydrogen abstraction mechanism is a common photochemical reaction, especially observed in polymers like PS when exposed to UV radiation.[9] During the UV irradiation, hydrogen atoms are abstracted from the main chain -CH_2 groups. The absence of -OH signals indicate that adipic acid and itaconic acid may are being decomposed during the irradiation, and responsible for the H-abstraction in the polymeric chain. This abstraction generates a reaction site, which in other conditions could lead to chain cleavage, but the presence of lignin during the irradiation leads to the grafting in the polymeric chain.

GPC analysis shows that in general, the polymeric chain does not suffer degradation due the UV radiation. GPC curves (data not shown) indicate that there is no formation of low weight products, which could justify PS chain cleavage.[15] In fact, the peak maximum is shifting to low retention time without any new bands or peaks. Table 1 shows the GPC data for PS, LO, and PS/LO samples. Is possible to observe that samples AA2, AA10, AA20, and AA50 showed a reduction in Mw and Mn values when comparing with pristine PS. The same samples slightly increased PDI value. This data could indicate that in those samples, the H-abstraction could lead to main chain cleavage, but the presence of lignin confirmed on the spectroscopic analysis, indicates that the cleavage is followed by the grafting of lignin units, which could also explain the low reduction of Mn and Mw values. AA5, AA50, IA2, IA10, IA20, and IA50 show the opposite behaviour. For these samples the values of Mw and Mn increase and the value of PDI decrease. For those samples, the cleavage is not evident in the GPC data, and the results also agree with the spectroscopic analysis. The grafting of LO units could lead to an increase in the Mw and Mn values. The presence of grafted lignin units could cause crosslinking between chains, which explains the decrease of PDI values.[16] The strain-stress data was obtained using an elongation test. The results of tensile strength (at breaking point) and the Young's modulus (E) are presented in Table 1. The tensile strength value of pristine PS was 21.78 MPa, and Young's modulus value was 2.33 GPa. All composites present a reduction in the tensile strength value. The tensile strength value of AA5, AA10, and AA20 composites do not suffer significant reduce (Table 1). A considerable reduction occurs with AA50. AA5, AA10, and AA50 showed a small increase in the value of Young's modulus.

Toriz et al. produced lignin/PP composites and reported that the effects of adding lignin to PP resulted in a decrease of the tensile strength value, proportional to the quantity of lignin added.[17] A reduction in the tensile strength is usually due to a partial interaction between load particles and the matrix. AA samples, in general, have little variation in the tensile strength value which can be correlated with the grafting of lignin macromolecules onto the polymeric chain. Once the PS/LO composite is formed the grafted lignin domains will stabilise non-grafted lignin domains. The better interaction reflects on the tensile strength results.[18] The tensile strength value of AA50 indicates that high concentration of lignin (50%) cannot be stabilised by the PS matrix, reducing the interaction between non-grafted lignin domains and composite chains. For IA samples, the tensile strength values decrease considerably.

Table 1. GPC data (Mn, Mw, and PDI) and mechanical test (tensile strength and Young's modulus for starting materials (PS and LO) and composites (AA and IA), and EDS data (carbon and oxygen) of starting materials (PS and LO) and all PS/LO composites.

Sample	**Mn (Da)**	**Mw (Da)**	**PDI (a.u.)**	**Tensile Strenght (MPa)**	**E (GPa)**	**EDS analysis**	
						Carbon (%)	Oxygen (%)
PS	93,126	221,063	2,3	21.78 (±0.02)	2.33	97.8	2.2
LO	1,222	2,067	1,6	-	-	50.6	49.4
AA2	89,061	216,421	2,4	18.65 (±0.05)	1.82	98.9	1.1
AA5	97,866	208,660	2,1	21.00 (±0.02)	2.57	88.6	11.4
AA10	79,816	186,097	2,3	19.65 (±0.02)	2.45	97.7	2.3
AA20	82,299	199,861	2,4	21.63 (±0.01)	1.95	96.6	3.4
AA50	92,511	219,125	2,3	6.18 (±0.03)	2.45	85.3	14.7
IA2	98,805	218,898	2,2	17.76 (±0.07)	2.41	90.3	9.7
IA5	85,340	208,354	2,4	16.93 (±0.06)	1.81	95.3	4.7
IA10	101,764	215,441	2,1	16.32 (±0.02)	2.48	71.5	28.5
IA20	105,796	223,164	2,1	17.06 (±0.02)	2.31	78.4	21.6
IA50	102,670	218,611	2,1	6.56 (±0.01)	1.54	96.5	3.5

When compared with PS data, with the exception of sample IA5, all IA samples show an increased Mn value and a decreased PDI value. The itaconic acid molecule has three chromophores groups. During the irradiation, the molecule could have a more efficient H-abstraction capability when compared with adipic acid. The IA composites could have a higher possibility of crosslinking between the polymeric chains than the AA coomposites, resulting in a superior hardness of the material. EDS and SEM analysis were performed on all samples. Table 1 shows the semi-quantitative data of carbon and oxygen percentage for pristine PS, LO and all composites prepared with adipic acid and itaconic acid. This comparison was possible due to the different carbon/oxygen ratio between LO and PS. As can be noted in Table 1, PS has in its composition 98.8% of carbon and 2.2% of oxygen. Post-consumer PS presents a low oxygen content due to the addition of plasticisers during processing and manufacturing. On the other hand, LO presents in its composition 50.6% of carbon and 49.4% of oxygen.

After the photochemical reaction, for the AA samples, it is possible to observe an increase in the amount of oxygen, with the exception of AA2. AA5 was the smaple which presented the biggest oxygen content (11.4%). AA20 had a slight increase (3.4%) when comparing with pristine PS. Table 1 also shows the data for the IA composites which shows an increase in the oxygen percentage for all samples. IA2, IA10, and IA20 presented the highest values. IA5 and IA50 the lowest values, however, when compared with PS, the oxygen content still increased.

Comparing the EDS data with the previous discussion it is possible to observe some interesting correlations. The composites which presented the lowest oxygen content (AA2, AA10, IA5, and IA50), when compared with PS, also presented in the majority, a reduction in the Mn, Mw, tensile strength, Young's modulus and increase in PDI. Low presence of oxygen can be linked with the less grafting of lignin onto PS chains. It is likely that the number of grafted domains were not enough to provide stability for the non-grafted lignin. In those samples, there is the formation of pure lignin microdomains, leading to phase separation.

All samples with the highest oxygen content also presented an increase in the values of Mn, Mw, Young's modulus, and a small decrease in the tensile strength and PDI values. In those samples, the number of grafted lignin macromolecules were probably enough to stabilise the amount of non-grafted lignin.

The tendency observed above also repeats in SEM analysis. Figure 2 shows SEM images of the PS films, LO aggregates, and four composites (AA5, AA20, IA5, and IA50). As can be observed in Figure 2, PS films have a typical smooth surface, even at a magnification of 40.000x. LO does not form films, but particle aggregates. AA5 and AA20 keep the same smooth characteristic, with no sign of degradation, cracks, holes or particles. The same occurs for IA2, IA10, and IA20 (supporting information). This homogeneous appearance is related to mechanical properties and also with non-degraded chains[8] .

Wang et al., grafted chemical modified lignin in PS obtained films with great resemblance to the PS/LO films obtained in this work. The authors state that the smooth characteristic is due the good interaction between lignin monomers and grafted chains.[19]

Figure 2 also shows IA5 and IA50 images, which do not present the same film homogeneity. As can be observed, the IA5 image presents spots, particles, and dark marks (possible cracks) in the film surface. Similar features can be observed in the IA50 image (Figure 2) and in this case, a circular area corresponds to a lignin domain. EDS analysis reveals that inside the microdomain (circle) the carbon and oxygen percentage are very similar to the lignin values, while outside the microdomain the carbon and oxygen percentage matches with the composite IA50 values in Table 1.

These images confirm the spectroscopic, chromatographic, and mechanical data. In general, a short time of UV-radiation exposure in the presence of adipic acid and itaconic acid is enough to graft LO macromolecules into the PS polymeric chain.

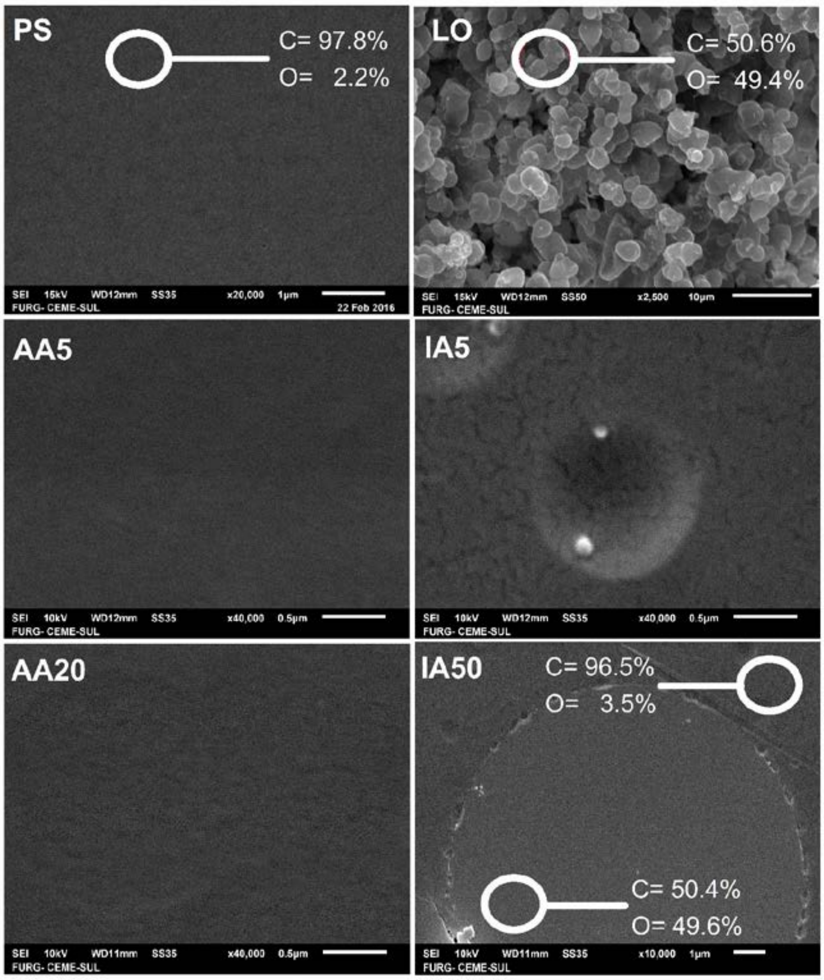

Figure 2. MEV images of PS, LO composite AA5, composite IA5, composite AA20, and IA50. PS, LO and IA50 presents carbon and oxygen composition provided by EDS analysis.

The formed films present spectroscopic data that confirm the presence and relative integrity of PS and LO macromolecules. The AA5 and AA20 composites results in uniform and transparent films that in overall maintain PS mechanical characteristics. Similar characteristics were obtained for IA2, IA10 and IA20 composites.

4. CONCLUSIONS

The changes observed in the FTIR-ATR spectra confirm the presence of lignin in the composites samples and also changes in the PS polymeric chain. GPC data presents changes in the molar mass, where it was possible to confirm the FTIR analysis. GPC data also relates to the mechanical tests, where for IA and AA samples, the tensile strength values decrease considerably, and discrete oscillation of the Young's modulus when compared with pristine PS. EDS data and MEV images showed that the samples have different oxygen contents, and it seems to be related to the mechanical properties. When the composites presented a low oxygen content, the mechanical properties seem to be worse than pristine PS. When the composite presented an increase in the oxygen content, the mechanical properties seem to be slightly improved. The methodology described in this article could be applied to different post-consumer polymers and showed to be a very interesting green chemical route to generate new materials from polymeric residue and industrial waste.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Brazilian agencies CNPq and CAPES. The authors deeply thank Professor V. G. Carratu and L. Bresolin for providing their equipment, also the Electron Microscopy Center - FURG (CEME-SUL), the Analytical Center – UFRGS, and the Laboratory of Food Technology (LTA - FURG).

REFERENCES

[1] W. Yue, P. Yao and Y. Wei, *Polymer Degradation and Stability*, 2009, **94**, 851-858.
[2] J. Zhao, Q. Shi, S. Luan, L. Song, H. Yang, H. Shi, J. Jin, X. Li, J. Yin and P. Stagnaro, *Journal of Membrane Science*, **369**, 5-12.
[3] Z. Zhang, Y. Lai, L. Yu and J. Ding, *Biomaterials*, 2010, **31**, 7873-7882.
[4] N.-F. Chiu and T.-Y. Huang, *Sensors and Actuators B: Chemical*, 2014, **197**, 35-42.
[5] W. Dai, L. Yu, Z. Li, J. Yan, L. Liu, J. Xi and X. Qiu, *Electrochimica Acta*, 2014, **132**, 200-207.
[6] J. Gu, J. Du, J. Dang, W. Geng, S. Hu and Q. Zhang, *RSC Advances*, 2014, **4**, 22101-22105.
[7] H. Zhao, B. Zhu, J. Sekine, S.-C. Luo and H.-h. Yu, *ACS Applied Materials & Interfaces*, 2012, **4**, 680-686.
[8] I. Rodriguez, L. Shi, X. Lu, B. A. Korgel, R. A. Alvarez-Puebla and F. Meseguer, *Nanoscale*, 2014, **6**, 5666-5670.
[9] R. Rajajeyaganthan, F. Kessler, P. H. de Mour Leal, S. Kühn and D. E. Weibel, *Macromolecular Symposia*, 2011, **299-300**, 175 182.
[10] T. Zhang, X. Li and H. Gao, *Journal of the Mechanics and Physics of Solids*, 2014, **67**, 2-13.
[11] Rosa, M. P; Beck, P. H.; Muller, D. G.; Moreira, J. B.; Silva, J. S.; Durigon, M. M. . *Biological and chemical research*, v. 4, p. 87-98, 2017.
[12] Y. Yamada, K. Murota, R. Fujita, J. Kim, A. Watanabe, M. Nakamura, S. Sato, K. Hata, P. Ercius, J. Ciston, C. Y. Song, K. Kim, W. Regan, W. Gannett and A. Zettl, *Journal of the American Chemical Society*, 2014, **136**, 2232-2235.
[13] W. Zhang, L. Qin, R.-R. Chen, X.-W. He, W.-Y. Li and Y.-K. Zhang, *Applied Surface Science*, **256**, 3000-3005.
[14] W. Wang, R. M. T. Griffiths, A. Naylor, M. R. Giles, D. J. Irvine and S. M. Howdle, *Polymer*, 2002, **43**, 6653-6659.
[15] C. Zhijiang, H. Chengwei and Y. Guang, *Polymer Degradation and Stability*, 2011, **96**, 1602-1609.
[16] J. Zhou, Y. Hu, X. Li, C. Wang and L. Zuin, *RSC Advances*, 2014, **4**, 20226-20229.
[17] M. Zelzer, M. R. Alexander and N. A. Russell, *Acta Biomaterialia*, 2011, **7**, 4120-4130.
[18] H. Qin, Y. Xu, J. Kim, T. Hwang and T. Kim, *Materials Science and Engineering: B*, 2014, **184**, 72-79.
[19] L. Feng and B. I. Suh, *Macromolecular Chemistry and Physics*, 2007, **208**, 295-306.