Hydrogen peroxide/UV treatment on polylactide/polyurethane blends for biomedical applications

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Abstract

Biodegradable polymers should be non-toxic, possess low immunogenicity and good mechanical properties. Due to their hydrophobicity and their low surface energy cells only poorly attach, spread and proliferate on these biodegradable polyesters. Therefore, the surface of these polyesters should usually be modified and already several approaches have been presented to increase their cell affinity. In this research the influence of hydrogen peroxide combined with ultra violet irradiation on wettability, morphology and mechanical properties of PU/PLA blends as well as their pure components. It was clearly visible that both pure PU and PLA acted completely different form PU/PLA blend during treatment. The wettability of pure polymers changed after H_2O_2/UV, PU surface became more hydrophilic, whereas PLA become slightly hydrophobic. Due to micropores and microcracks visible on surfaces resulted from breaking ester linkage, deterioration of their mechanical properties was also observed. The exposure of PU/PLA films to H_2O_2/UV irradiation showed the change of wettability toward more hydrophilic and increase of mechanical properties because of specific affinity to etching process.

Key words: hydrogen peroxide, UV irradiation, polylactide, polyurethane, surface modification, wettability, morphology, mechanical properties

Introduction

A biodegradable polymer is defined as a polymer that preserves its mechanical strength and other material performances during its practical application, but that is finally degraded to low molecular weight compounds such as H_2O, CO_2 and other non-toxic by products [1, 2]. An aliphatic polyester is a thermoplastic polymer which contains hydrolysable aliphatic ester linkage in its backbone [3, 4]. In theory all polyesters are degradable, however only aliphatic polyesters with reasonably short aliphatic chains between the ester bonds will degrade within a time interval suitable for biomedical applications [5]. Biodegradable polymers are non-toxic, possess low immunogenicity and good mechanical properties. Moreover, their degradation rate can be adjusted and therefore recently they have been extensively studied as scaffold matrices for tissue engineering [6-17]. Due to their hydrophobicity and their low surface energy cells only poorly attach, spread and proliferate on these biodegradable polyesters. Therefore, the surface of these polyesters should usually be modified and already several approaches have been presented to increase their cell affinity [18]. As most synthetic biodegradable polymers are rather hydrophobic, extensive efforts have thus been devoted towards increasing the biomaterial's hydrophilicity. Typically, they are chemically modified by introducing specific functional groups on their surface such as hydroxyl, carboxyl, amino and sulphate groups using different reaction gases such as air, NH_3, SO_2, CO_2 or other organic compounds [19]. Such techniques may possibly bring about disfavoured side effects such as rapidly occurring degradation process and deterioration of mechanical properties. Moreover, these modifying processes are thought to lead to irregular etching of the surface and their rate is dependent on physicochemical properties of used polymer (crystallinity, molecular weight, etc.) [18, 20].

The aim of the study was to determine the influence of hydrogen peroxide combined with ultra violet irradiation on wettability, morphology and mechanical properties of PU/PLA blends as well as their pure components.

Materials and Methods

Materials

Blends of polylactide and polyurethane as well as pure polymers were tested in this research. Both used polymers were of biomedical grade and were used without further purification. Polyurethane (PU) was purchased from GOY Bayer (Germany). PU molecules are built up of hexamethylenediisocyanate (HMDI) rigid segments, polycaprolactone (PCL) flexible segments and isosorbitol as a chain extender, shown in Fig.1. Polylactide (PLA), consisting of 80% poly-L-lactide and 20% poly-DL-lactide was puchased from Purac (Netherlands). The

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N,N–dimethylformamide (DMF) and hydrogen peroxide were analytical grade and purchased from POCh (Poland).

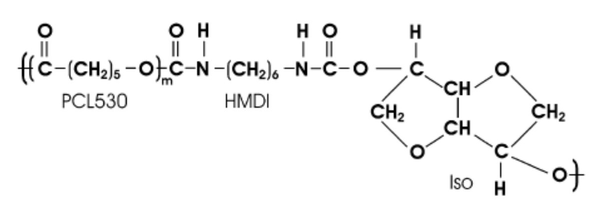

Figure 1. Chemical structure of polyurethane used in the study

Preparation

Blends of polylactide and polyurethane as well as pure polymers were tested in this research. Blends, pure PU, pure PLA samples were prepared by dissolving polymers in dimethylformamide to obtain a 10 wt. % solution. Weight ratio of PU to PLA was 4:1. The mixture was stirred with magnetic stirrer for at least 48h at ~50°C, and then cast on glass Petri dishes. The films were dried at 50°C under vacuum for 48 hours.

Hydrogen peroxide treatment

The specimens were immersed in a aqueous bath containing 30% w/v hydrogen peroxide at ambient temperature. They were kept in the bath for 1, 3 and 12 hours and dried in air under ultraviolet lamp.

Properties determination

The water contact angle of obtained PU/PLA and pure polymers films was measured using sessile drop method on Drop Shape Analysis System (DSA Mk2, Krüss, Germany). Ten measurements on each side of the film were accomplished. The data presented are average of ten measurements (± standard deviation).

Tensile strengths (TS), Young's moduli (E) and elongation at break (ε) of samples (70x5x0,2 mm) were measured using a universal testing machine (Zwick 1465, Germany) equipped with 1kN load cell. The sample length between the clamps was 45 mm and clamps' speed was 50 mm/min. The obtained results correspond to the average of ten measurements (± standard deviation).

The morphology of elaborated materials was evaluated using scanning electron microscopy (Nova Nano SEM 200, FEJ Europe). Prior to observations, materials were dried and sputtered with carbon.

Results and Discussion

The values of water contact angle of binary PU/PLA blends as well as pure polymers are presented in Table 1. The surface of pure polylactide is slightly hydrophobic (Θ~81°), but surfaces of pure polyurethane and blend are more hydrophobic, contact angle of both is slightly higher than 90°**.**

The hydrogen peroxide/UV irradiation treatment of pure PU caused significant changes. During photooxidation the its contact angle started decreasing, the longer treated, the more decreased and finally reached 36,8°. The surface became very hydrophilic, as presented in Fig. 2. It might be connected with etching process of less resistant segments of polyurethane, namely, soft segments consisting of polycaprolactone (PCL). PCL is semi-rigid aliphatic polyester, which may partially decompose in hydrogen peroxide and/or UV.

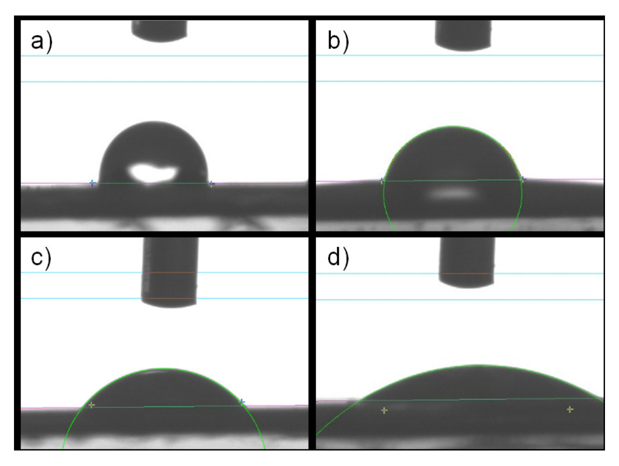

Figure 2. Drop shape of pure PU a) untreated, b) treated with hydrogen peroxide for 1h, c) treated with hydrogen peroxide for 3h and d) treated with hydrogen peroxide for 12h

The wettability of pure PLA has changed significantly. Firstly, the water contact angle decreased, but further hydrogen peroxide/UV treatment led to higher contact angle and surface became slightly hydrophobic, as presented in Fig. 3. It can be explain by the fact that PLA is a polyester, which is less resistant to aggressive and oxidizing H_2O_2 environment and in turn resulted

Table 1. Water contact angle (θ) of untreated and treated PU, PLA and PU/PLA films for 1h, 3h and 12h.

	Θ [°]			
	untreated	**after 1h**	**after 3h**	**after 12h**
PU	96,5±1,9	86,1±3,5	54,5±8,5	36,8±2,0
PLA	81,3±4,9	71,1±2,2	85,4±2,7	91,6±1,5
PU/PLA	91,1±10,2	75,3±7,7	67,9±12,0	60,5±6,8

in scission of ester linkage, and then degrade. It was attributed to significant contribution of nonpolar component rather than polar component resulting from the surface photooxidation of PLA [21, 22].

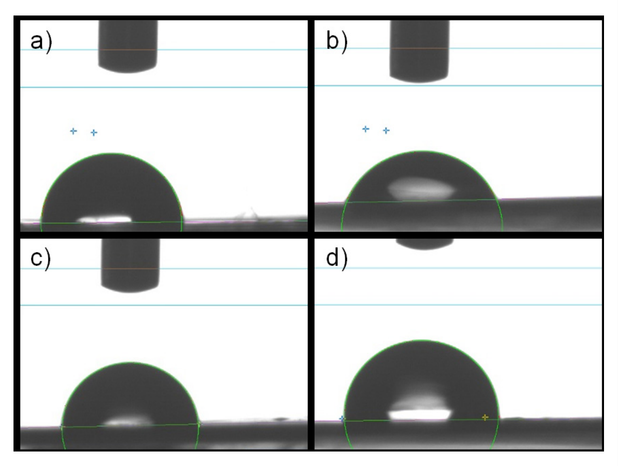

Figure 3. Drop shape of pure PLA a) untreated, b) treated with hydrogen peroxide for 1h, c) treated with hydrogen peroxide for 3h and d) treated with hydrogen peroxide for 12h

The contact angle of PU/PLA blend is a combined behaviour of its component. As it was expected, blend consists of 80% PU and 20% of PLA, thus, the surface is more similar to PU. Moreover, during treatment blend became also hydrophilic, as shown in Fig. 4. Fortunately, the scission effect of PLA linkage is less noticeable. The wettability level (θ~60°) of PU/PLA blend seems to be appropriate, because both highly hydrophilic and highly hydrophobic surfaces are not favourable for cell attachment. Surfaces with moderate wettability are able to adsorb proper amounts of adhesive proteins and at the same time enable to preserve their natural conformations, what stimulates positive cell response [19].

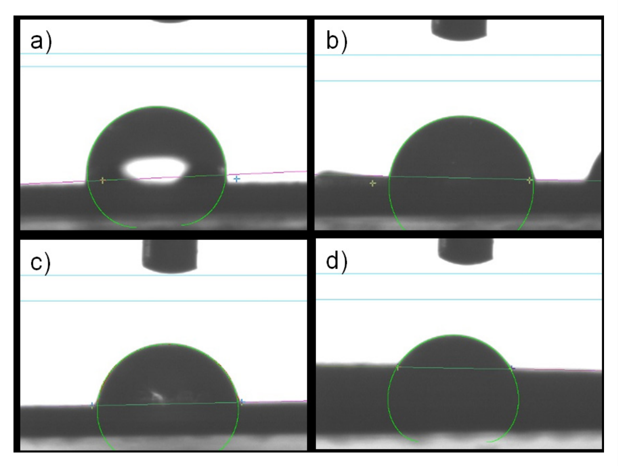

Figure 4. Drop shape of pure PU/PLA a) untreated, b) treated with hydrogen peroxide for 1h, c) treated with hydrogen peroxide for 3h and d) treated with hydrogen peroxide for 12h

Some groups have studied the interactions of different types of cultured cells or blood proteins with various solid substrates (mainly polymers) with different wettabilities to correlate the relationship between surface wettability and cell or blood compatibility. One main problem is that the surfaces are heterogeneous both chemically and physically (different surface chemistry, charge, roughness, rigidity, crystallinity, etc.), which may result in considerable variation. Moreover, method of manufacturing can also influence it, thus makes it more difficult to compare with other measurements.

Mechanical properties of PU/PLA and pure polymers are shown in Fig. 5. Exposure of both pure polymers samples to H_2O_2/UV resulted in significantly decreasing in tensile strength, elongation at break and Young's modulus. It is connected with above-mentioned scission of ester linkage in PLA and PCL, which PU soft segments are built up of, leading to molecular weight decrease. Treatment of PLA films for longer time than 1h caused a great growth of brittleness and rigidity, which precludes us from doing further mechanical tests. The mechanical properties of PU/PLA blend increased after H_2O_2/UV treatment.

The tensile strength increased by 326%, elongation at break increased by 173% and Young's modulus increased by 423%. This phenomenon might be connected with distribution of amorphous and crystalline regions of PLA and PU. It might be assumed that more resistant to H_2O_2/UV parts of both polymers, namely, hard HMDI segment from polyurethane and crystalline region from polylactide, were located in inner parts of obtained films, but these less resistant regions were located just at surface. Hence, only these could have been etched by hydrogen peroxide/UV and within the exposure time more amorphous region have been removed, thereby, mechanical parameters increased.

Observation under SEM shows that both pure PU and PLA surfaces have similar structure, as shown on Fig. 6 a-h. However, some micropores and microcracks are noticeable on their surface exposed to hydrogen peroxide/UV treatment. The formation of microcraks might be connected with the chain scission reaction, which took place in photodegraded samples. Breaking of polymer bonds produces fragments which need more volume than the original macromolecules. This causes strains and stresses which can be responsible for the formation of microcracks and damage, leading to deterioration of mechanical properties. Other reason of occurring micropores is method of sample preparation. Films obtained by solvent-casting may possess more or less regularly spaced micropores, depending on the solvent used. Pore size is dependent on the affinity between the polymer and solvent. Some agglomeration of granules on untreated PU/PLA surface is clearly visible. However, exposure to hydrogen peroxide/UV treatment removed all irregularities, firstly these with bigger diameter, then with smaller ones, as visible on Fig. 6 i, j and k.

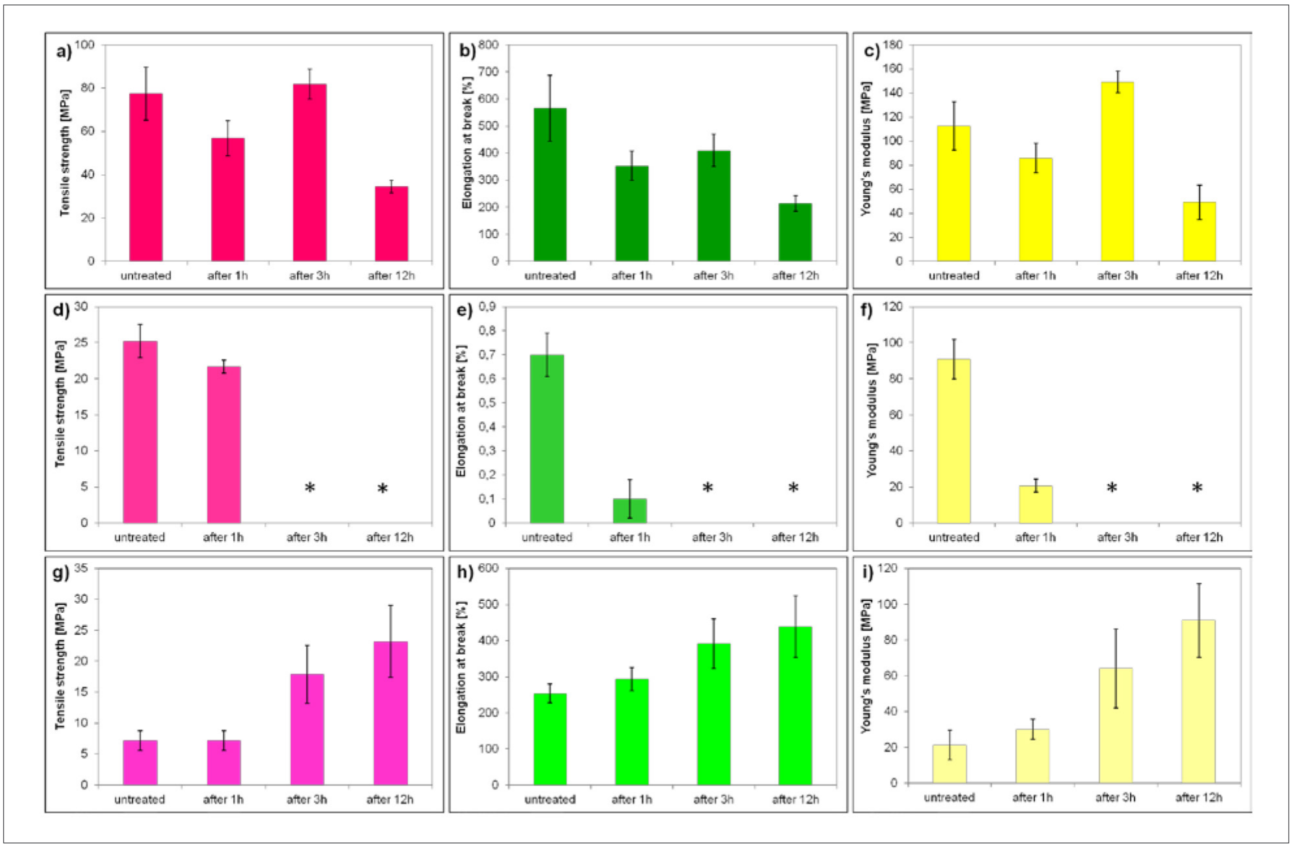

Figure 5. Effect of hydrogen peroxide/UV treatment on mechanical properties of pure PU (a), b), c)), of pure PLA (d), e), f)) and of PU/PLA (g), h), i)). Asterisks indicates the mechanical properties were below limit of detection of used equipment

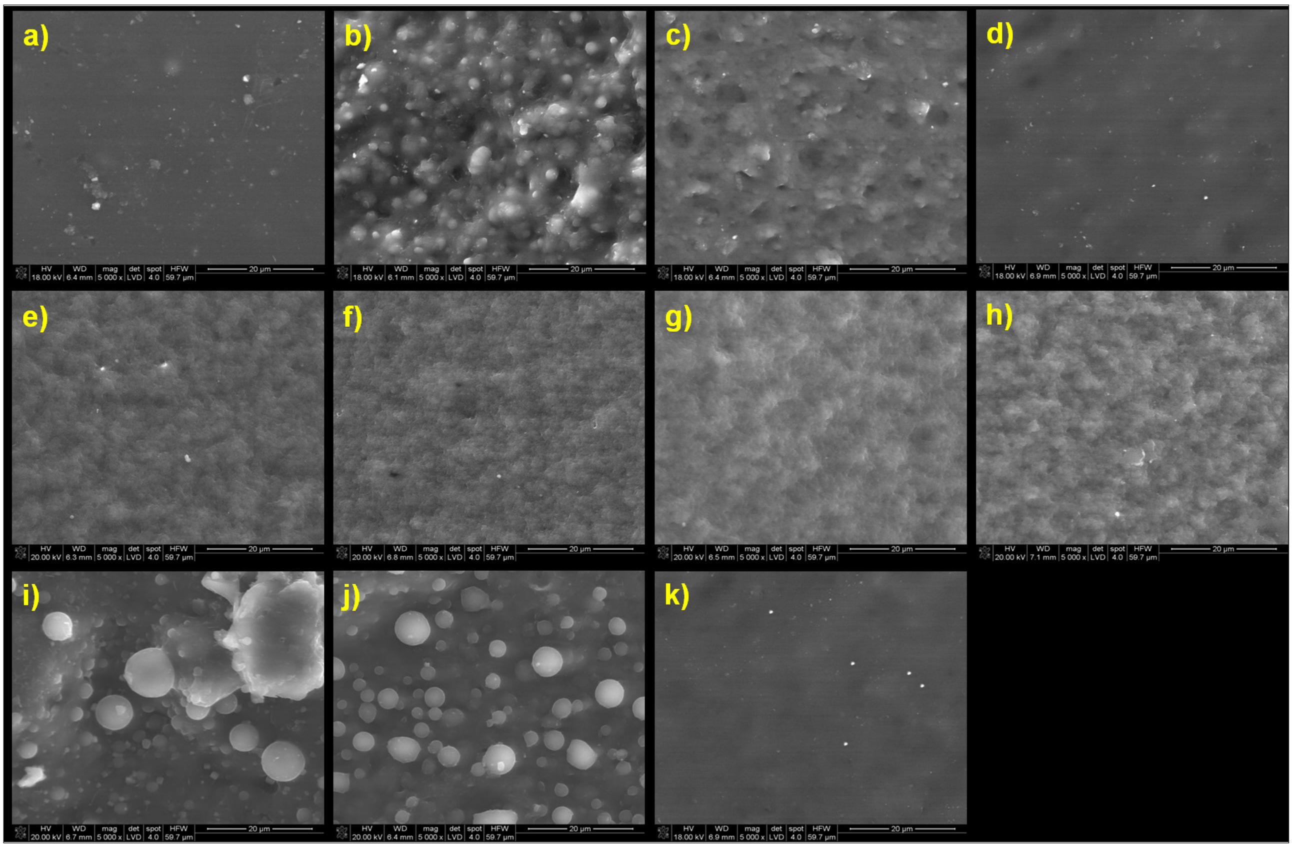

Figure 6. SEM images of pure PU (a) untreated, b) after 1 h, c) after 3 h, d) after 12 h), pure PLA (e) untreated, f) after 1 h, g) after 3 h, h) after 12 h) and of PU/PLA (i) untreated, j) after 1 h, k) after 3 h) hydrogen peroxide/UV treatment

Conclusions

Here H_2O_2 together with UV irradiation acts as an etching agent, but also as a source of additional hydrophilic side group. It should be mentioned that etching of the polymer surface by solvents, acids or oxidants is a technique used to reveal details of the internal structure. In the case of crystalline polymers, etching allows the removal of amorphous or semi-crystalline region from the surface, and the crystalline phase can be observed. It is known that photodegradation starts preferentially in the amorphous part, and then the crystalline region is ultimately degraded. The destruction of a dense, well-ordered phase needs more energy, which can be gained only after longer irradiation time. It was clearly visible that pure PU and PLA acted completely different form PU/PLA blend during treatment. The wettability of pure polymers changed after H_2O_2/UV, PU surface became more hydrophilic, whereas PLA become slightly hydrophobic. Due to micropores and microcracks visible on surfaces resulted from breaking ester linkage, deterioration of their mechanical properties was also observed. The exposure of PU/PLA films to H_2O_2/UV irradiation showed the change of wettability toward more hydrophilic and increase of mechanical properties because of specific affinity to etching process.

References

1. Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117–132.
2. J. C. Middleton and A. J. Tipton, *Biomaterials*, 2000, **21**, 2335–2346.
3. P. A. Gunatillake, R. Adhikari and N. Gadegaard, *Eur. Cells Mater.*, 2003, **5**, 1–16.
4. I. Vroman and L. Tighzert, *Materials (Basel).*, 2009, **2**, 307–344.
5. L. S. Nair and C. T. Laurencin, *Prog. Polym. Sci.*, 2007, **32**, 762–798.
6. H. Shen, X. Hu, F. Yang, J. Bei and S. Wang, *Biomaterials*, 2007, **28**, 4219–4230.
7. L. H. Chan-Chan, R. Solis-Correa, R. F. Vargas-Coronado, J. M. Cervantes-Uc, J. V. Cauich-Rodríguez, P. Quintana and P. Bartolo-Pérez, *Acta Biomater.*, 2010, **6**, 2035–2044.
8. Q. Liu, L. Jiang, R. Shi and L. Zhang, *Prog. Polym. Sci.*, 2012, **37**, 715–765.
9. Z. Zhang, R. Kuijer, S. K. Bulstra, D. W. Grijpma and J. Feijen, *Biomaterials*, 2006, **27**, 1741–1748.
10. P. Mainil-Varlet, B. Rahn and S. Gogolewski, *Biomaterials*, 1997, **18**, 257–266.
11. H. S. Azevedo and R. R. L. Reis, *Biodegrad. Syst. tissue*, 2005, 177–202.
12. A. G. M. Lu, Lichun, Charles A. Garcia, *J. Biomed. Mater. Res.*, 1999, **46**, 236–244.
13. M. Meek, K. Jansen and R. Steendam, *Res. Part A*, 2004.
14. T. Xi, M. Sato, A. Nakamura and Y. Kawasaki, 1994, **28**, 483–490.
15. A. C Albertsson and M. Eklund, *J. Appl. Polym. Sci.*, 1995, **57**, 87–103.
16. Q. Liu, J. Wu, T. Tan, L. Zhang, D. Chen and W. Tian, *Polym. Degrad. Stab.*, 2009, **94**, 1427–1435.
17. N. Murthy, S. Wilson and J. C. Sy, *Polym. Sci. A Compr. Ref. 10 Vol. Set*, 2012, **9**, 547–560.
18. T. Desmet, R. Morent, N. De Geyter, C. Leys, E. Schacht and P. Dubruel, *Biomacromolecules*, 2009, **10**, 2351–2378.
19. Z. Ma, Z. Mao and C. Gao, *Colloids Surfaces B Biointerfaces*, 2007, **60**, 137–157.
20. J. M. Goddard and J. H. Hotchkiss, *Prog. Polym. Sci.*, 2007, **32**, 698–725.
21. G. H. Koo and J. Jang, *Fibers Polym.*, 2008, **9**, 674–678.
22. M. H. Ho, J. J. Lee, S. C. Fan, D. M. Wang, L. T. Hou, H. J. Hsieh and J. Y. Lai, *Macromol. Biosci.*, 2007, **7**, 467–474.