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In-line monitoring of the thermal degradation of poly(L-lactic acid) during melt extrusion by UV–vis spectroscopy

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Abstract

Melt processing of poly(L-lactic acid) (PLLA) can lead to both molar mass reduction and colour formation, which can alter properties critical for medical applications (e.g. biodegradation rate). In this work, ultra-violet/visible (UV–vis) spectroscopy was applied to in-line monitor the extrusion of PLLA on a co-rotating twin screw extruder. Molar mass, viscosity and *in vitro* biodegradation behavior of the extrudates were analyzed off-line. UV–vis spectroscopy turned out to be very sensitive to minute colour changes of the melt. For dry PLLA a clear correlation between increasing UV–vis absorption of the melt and molar mass reduction of the extrudates is found. From the dependence of molar mass reduction on processing conditions it is concluded that thermal degradation dominates. The heat input bases on direct heating and on conversion of mechanical energy. The presence of moisture in the polymer does not significantly influence the UV–vis spectra but contributes to further molar mass reduction. *In vitro* biodegradation of extruded dry PLLA shows that processing parameters have an influence on the biodegradation behavior. A good correlation between the biodegradation rate of the extrudates and the UV–vis absorption of the melt is found. This investigation demonstrates that UV–vis spectroscopy is powerful for real time detecting the thermal degradation of PLLA during melt extrusion.

Keywords: Polylactic acid; Thermal degradation; Biodegradation

1. Introduction

Poly(L-lactic acid) (PLLA) is a well-known biodegradable and biocompatible polymer. It has received much interest for its medical and pharmaceutical applications, such as suture, orthopaedic devices, scaffolds for tissue engineering and drug delivery systems [1–5].

The PLLA implant devices are usually produced by melt processing techniques, such as extrusion and injection moulding [6,7]. Due to its thermal unstable nature [8,9], a reduction in molar mass occurs during processing. This leads to altering of properties critical to the biodegradation rate, mechanical properties and cell response of PLLA [10–15]. Another process-limiting phenomenon associated with the upper limit of thermal processing is the development of colour in PLLA when processed above its melting temperature [16]. This adversely affects the properties and end use of the final product making it suitable only for low-grade materials or where colour is not an issue. As a matter of fact, discolouring has been considered as one of the most critical problems that arise during melt processing of aromatic polyesters, including poly(ethylene terephthalate) [17,18] and poly(trimethylene terephthalate) [19].

The influence of processing parameters on the degradation of PLLA during extrusion has been evaluated off-line by determination of the molar mass, the thermal (glass transition) and mechanical properties of the extrudates [15]. The off-line experiments are time consuming, but crucial in determining the influence of processing on the resulting properties. Minimizing off-line measurements and replacing them with real time monitoring using in-line instrumentation will give insight into the thermal degradation of PLLA while it is being processed. Ultra-violet/visible light (UV–vis) spectroscopy,

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which is very sensitive to colour formation, has been proved to be a suitable method for *in situ* monitoring of polymer degradation in a laboratory setup [20,21]. In parallel, other techniques such as near-infrared (NIR), Raman and ultrasound spectroscopies have been successfully applied during extrusion for in-line monitoring chemical and morphological characteristics in the melt of different polymer systems, showing the advantages of rapid, reliable, non-invasive and cost effective analyses [22–24]. In this study, we applied the UV–vis spectroscopy technique for monitoring the process induced degradation of PLLA during extrusion. The results shall help to produce biomedical and pharmaceutical parts with reliable quality.

2. Experimental

2.1. Material and conditioning

PLLA was supplied in granules by Biomer, Germany. After dried at 100 °C for 3 h, the granules were either processed immediately or conditioned prior to extrusion for 24 h at 20 °C and a relative humidity of 51%.

2.2. In-line measurements

The extrusion was performed using a co-rotating twin screw extruder HAAKE PolyLab system (PTW 16/25; Thermo Electron Corporation) equipped with a vacuum degassing unit. The polymer was fed automatically. The influence of the processing parameters barrel temperature, screw speed and throughput was investigated. The barrel temperature was either 180 or 200 °C. The feeding zone was kept at a temperature of 15 °C below the barrel temperature. The screw speed was 20, 50, 100, 200, 300 or 400 rpm, respectively. The throughput was set to 0.2, 0.34 or 0.61 kg/h, respectively. Torque data were electronically logged and stored.

A special measurement slit die was flange connected to the extruder immediately behind the screw tips. Within that die the melt is flowing through a channel with rectangular cross-section (width 20 mm, height 4 mm). UV–vis transmission (sample thickness of 4 mm) probes were fitted to the melt channel. Additionally, NIR transmission probes and a probe for Raman spectroscopy, as well as pressure transducers and a melt temperature sensor were installed (Fig. 1a). The spectroscopy probes were connected to the corresponding spectrometers (Fig. 1b) via optical fibres. The optical fibres cause a cut-off at a wavelength of roughly 280 nm for the UV–vis spectra. The UV–vis spectrometer was a MultiSpec 2-channel process spectrometer system (tec5 AG, Germany). The NIR and Raman spectra were recorded by a SentroProc NIR/RAMAN process spectrometer (Sentronic GmbH, Germany). In the following only the UV–vis spectra will be discussed, since the NIR and Raman spectra as well as pressure changes are of minor significance.

For each set of processing parameters (temperature, screw speed and throughput) samples of the extruded melt strand were taken during stationary state. These samples were analyzed further by off-line analytics.

To determine the residence time a pellet of a red colour master batch was added to the feeding during stationary state. The dye exhibits an absorption maximum at 555 nm. Recording the absorbance at that wavelength as function of time after the pellet had been added, immediately delivers the residence time distribution. The time corresponding to the occurrence of the absorbance maximum is taken as measure of the residence time.

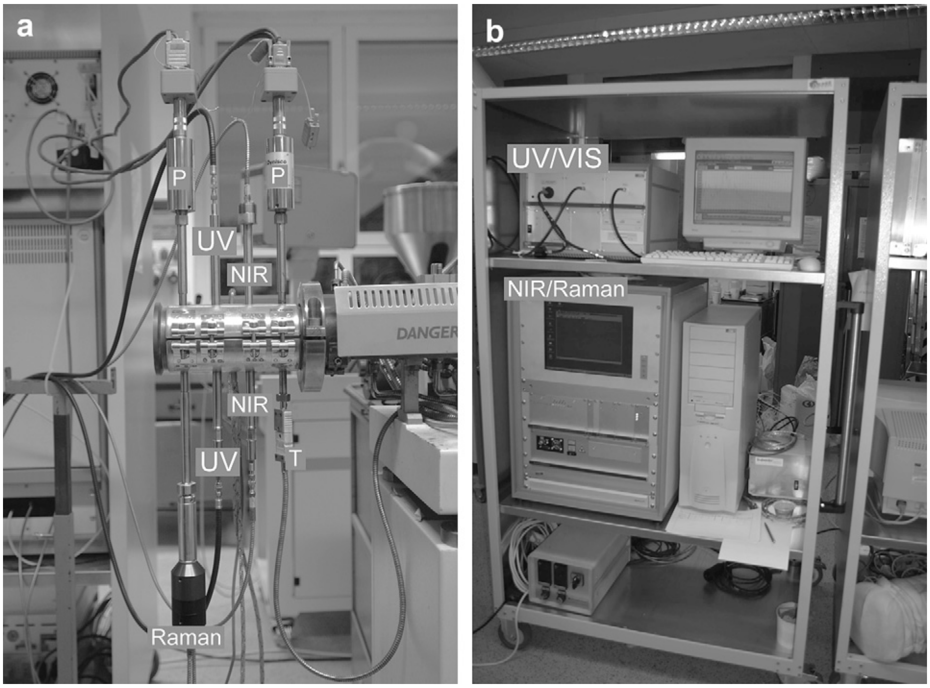

Fig. 1. (a) Measurement die equipped with probes for optical spectroscopy, pressure and temperature, and (b) process spectrometers.

2.3. Off-line measurements

2.3.1. Molar mass determination

The molar masses of the PLLA samples were determined by size exclusion chromatography (SEC, GPC) in THF using toluene as internal flow marker. The GPC-setup consisted of a Waters 515 isocratic HPLC pump, a TSP AS 100 autosampler, a Waters UV 486 Detector operated at 254 nm and a Waters 410 differential refractometer. Three SDV columns (PSS, Polymer Standards Service GmbH, Mainz, Germany) with nominal pore sizes of 10^6, 10^5 and 10^4 Å (30 × 0.8 cm each) were used. Calibration was performed using narrow distributed polystyrene standards. Data acquisition and processing was performed using PSS WINGPC software (version 6.2). The normalized number-averaged molar mass of PLLA was calculated according to $M_n/(M_n)_o$, where M_n is the number-averaged molar mass of extruded PLLA, and $(M_n)_o$ is the number-averaged molar mass of PLLA as received but ried. The measured $(M_n)_o$ was 1.25×10^5 g/mol, which was higher than the M_n values of the extrudates processed at various conditions. The polydispersity index M_w/M_n corresponding to $(M_n)_o$ was 1.98. The polydispersity index of the extrudates was in the range of 1.63–2.50. No clear influence of the processing parameters on the polydispersity was observed. Therefore, only the influence of processing parameters on the number average molar mass of PLLA will be discussed in the following.

2.3.2. Melt viscosity

The dynamic melt viscosity (η) of the samples was measured utilizing a Rheometrics RDS II torsional rheometer with 7.9 mm stainless steel parallel plates under a nitrogen atmosphere. The temperature was 180 °C, applying 5% deformation with a frequency of 1 Hz.

2.3.3. In vitro biodegradation

Phosphate-buffered saline (PBS) tablets were purchased from Fluka Biochemika (# 79382). Each tablet was dissolved in 200 ml distilled water to obtain a solution consisting of 137 mM NaCl, 2.7 mM KCl and 10 mM phosphate buffer (pH 7.4 at 25 °C). Samples with weights ranging from 0.27 to 0.30 g were cut from extruded plates (ca. 2 mm thickness). The samples were separately immersed in 10 ml of PBS in a plastic tube sealed with a cap and incubated in an oven at 60 °C until removal at 2–16 weeks. The buffered solution was exchanged every 4 weeks.

At the end of each degradation time, the samples were removed from solution, rinsed with distilled water, dried in vacuum oven at 50 °C for 48 h and weighed, to determine the weight loss. The weight loss percentage was calculated as the ratio of the mass difference before and after degradation due to their original mass. Each data point was the average of three samples.

3. Results and discussion

3.1. Influence of processing conditions

Throughput, screw speed and processing temperature are the most important parameters for polymer extrusion. The influence of throughput on the UV–vis spectra and normalized molar mass $M_n/(M_n)_o$ of PLLA is shown in Fig. 2a and b, respectively. At constant processing temperature (200 °C) and screw speed (400 rpm), decreasing throughput increases the UV–vis absorption of the melt (Fig. 2a), while the molar mass of the extruded materials decreases (Fig. 2b). The decreasing molar mass clearly mirrors increasing degradation of the PLLA. The enhanced degradation with decreasing throughput can be explained considering two factors: First, at constant screw speed decreasing throughput causes increasing residence time: At 400 rpm and a throughput of 0.61 kg/h the residence time was 2.9 min. For the throughput of 0.2 kg/h an almost three times larger value for the residence time of 8 min was obtained. Longer residence time allows the degradation reaction to perform longer, therefore material having lower M_n will be formed. Second, at lower throughput the melt is exposed to shear and elongational deformations for longer times. This leads to additional heating by conversion of mechanical energy, which can cause additional thermal degradation. Simultaneously chain rupture might occur. From the spectra shown in Fig. 2a, we suggest that new chromophoric groups (double bonds) are formed in parallel to the molar mass reduction. The formation mechanism of the new chromophoric groups will be discussed in Section 3.3.

The UV–vis spectra and normalized molar mass of PLLA obtained at various screw speeds are shown in Fig. 3a and b, respectively. The barrel temperature was kept constant at

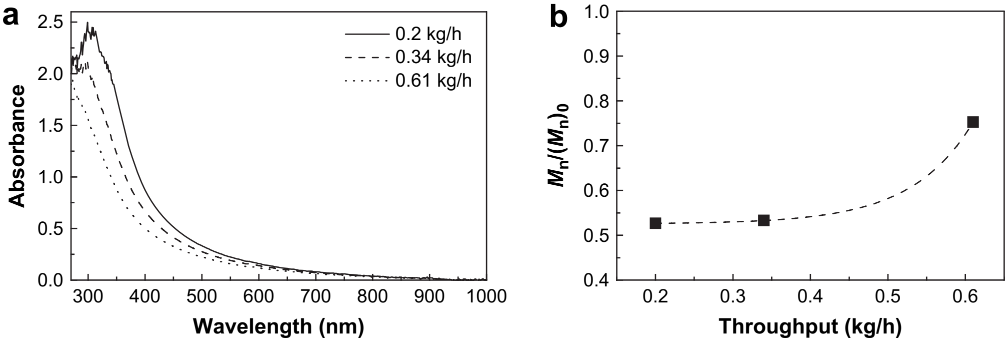

Fig. 2. Variation of (a) UV–vis spectra and (b) normalized molar mass as function of throughput at 200 °C and 400 rpm for PLLA (the dotted lines are guide for the eyes).

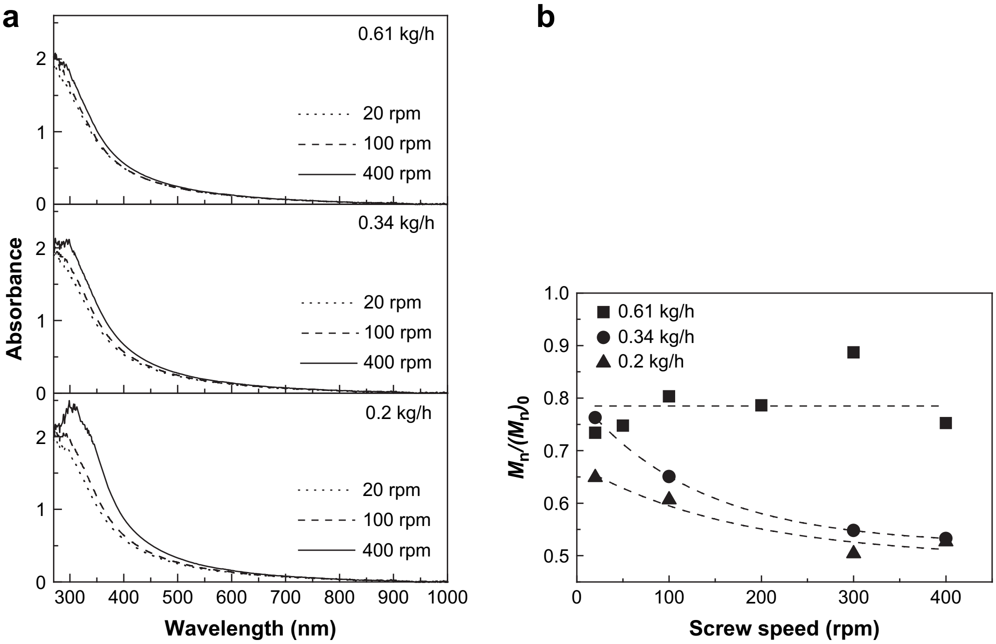

Fig. 3. Variation of (a) UV–vis spectra and (b) the normalized molar mass as function of screw speed at 200 °C and different throughput values of PLLA (the dotted lines are guides for the eyes).

200 °C and the throughput was set to three fixed values (0.61, 0.34 and 0.2 kg/h). All spectra show a continuous decrease of absorption with increasing wavelength. The small maxima which can be seen for the 400 rpm samples are in the wavelength range where the absorption of the optical fibres connecting the probes with the spectrometer becomes dominant. The resulting low count rate on the UV–vis diode array detector leads to a large error. Therefore, an interpretation of the maximum would be rather arbitrary. At constant temperature and throughput, increasing screw speed increases the UV–vis absorption of the melt (Fig. 3a). There is the trend, that increasing UV–vis absorption corresponds to decreasing molar mass of the extruded materials (Fig. 3a and b). Evidently, the influence of screw speed on the UV–vis spectra and the molar mass reduction is more pronounced for lower throughput. Increasing screw speed at constant throughput causes additional heating of the melt due to shear and elongational deformation. Most probably, the heat input due to conversion of mechanical energy is responsible for the screw speed-dependent degradation for throughputs of 0.34 and 0.2 kg/h. On the other hand, increasing screw speed tends to reduce residence time and degradation (see above). However, Fig. 3 shows increasing degradation with increasing screw speed. The increase of mechanical impact with increasing screw speed most likely overcompensates the effect of reduction of residence time. In deed, the reduction of residence time with screw speed is not much pronounced: For the throughput of 0.2 kg/h and screw speed of 100 and 400 rpm, respectively, the residence times were 10.5 and 8 min, respectively. For the throughput of 0.61 kg/h and the same screw speeds, the residence times were 3.9 and 2.9 min, respectively. This means, when the screw speed is increased by a factor of four, the residence time decreases only to about 3/4 of the value at lower screw speed. The finding that the residence time mainly is determined by the throughput and to less extent by the screw speed agrees with Ref. [25].

On the other hand, for the higher throughput (0.61 kg/h) no significant dependence of molar mass reduction on screw speed can be seen (Fig. 3b). Probably degradation is a highly non-linear process and below a certain value of the residence time (which decreases with increasing throughput) the degradation reaction is limited. The trend can be seen, that the molar mass of PLLA decreases with decreasing throughput for all screw speeds (Fig. 3b). This is in accordance with the discussion for Fig. 2b.

The mechanical energy impact due to shear and elongational deformation which can lead to both, temperature increase (see above) and/or chain rupture, is described by the specific mechanical energy (SME). For a deeper understanding on how throughput and screw speed influence the process induced degradation of PLLA, the values of the SME were evaluated using Eq. (1) [26]:

$$\mathrm{SME} = (2\pi\omega M)/\dot{m} \tag{1}$$

where ω is the screw speed (1/s), M is the torque (Nm) and $\dot{m}$ is the throughput (g/s). The unit of SME is J/g. In Fig. 4 the SME dependence of $M_n/(M_n)_o$ is plotted. The open symbols correspond to varying screw speed at a constant throughput of 0.2 kg/h. The data are taken from Fig. 3b. The solid squares are related to different throughputs at a constant screw speed of 400 rpm (data from Fig. 2b). Obviously, the degradation of PLLA is stronger for higher SME. Similar findings were reported for starch [26]. However, in the current study, the data point for 400 rpm and the throughput of 0.61 kg/h does not coincide with the curve for constant screw speed. This indicates that at higher throughput the SME based degradation is less

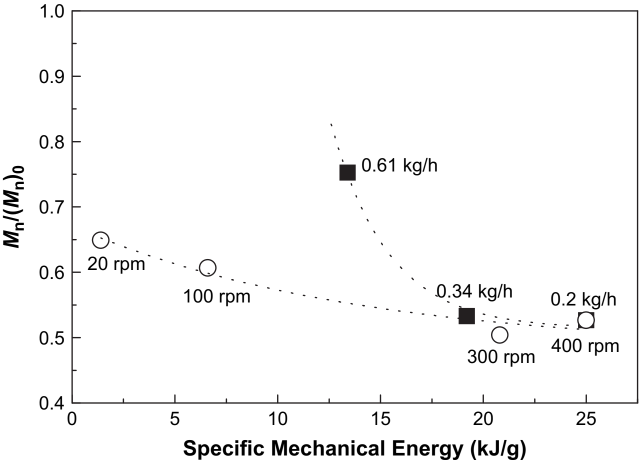

Fig. 4. The SME dependence of $M_n/(M_n)_o$ for a constant throughput of 0.2 kg/h and increasing screw speed (open circles), and for constant screw speed of 400 rpm and decreasing throughput (solid squares). The dotted lines are guides for the eyes.

pronounced for PLLA. This finding also agrees well with Fig. 3b, where for the high throughput of 0.61 kg/h no significant dependence of molar mass reduction with screw speed can be seen. As stated above, the residence time decreases by almost a factor of 3 when the throughput is increased from 0.2 kg/h to 0.61 kg/h. Therefore it can be concluded that the thermal degradation (related to residence time, which decreases with increasing throughput) at a given barrel temperature is dominating over the degradation by mechanical energy impact (related to screw speed).

Lower molar mass is usually related with lower viscosity. For instance, the dynamic melt viscosity of the PLLA as received but dried was around 4000 Pa, while a dynamic viscosity of around 1000 Pa was obtained for PLLA extruded at 200 °C, 400 rpm and 0.2 kg/h. The measurement conditions for the viscosity were 180 °C and 1 Hz in both cases.

The influence of processing temperature on the UV–vis spectra and normalized molar mass of PLLA is shown in Fig. 5a and b. The throughput was kept constant at 0.34 kg/h and the screw speed was fixed to different values from 20 to 400 rpm. At constant screw speed and throughput, increasing temperature causes increasing UV–vis absorption of the melt, while M_n of the extruded materials is decreasing. The decrease in M_n of PLLA with increasing temperature is consistent with literature [8,15]. It can be seen (Fig. 5b) that the influence of screw speed on the degradation of PLLA is more pronounced at 200 °C than 180 °C. This can be explained as follows. As discussed above, with increasing screw speed the temperature of the melt will increase (see e.g. [27]). Furthermore, the temperature dependence of the degradation rate of PLLA is non-linear and is described by the Arrhenius equation [28]. Therefore, the temperature increase caused by mechanical energy has more pronounced influence on the degradation of PLLA when processed at 200 °C than at 180 °C.

3.2. The influence of moisture

The influence of moisture in PLLA on the UV–vis absorption and the normalized molar mass is shown in Fig. 6a and b, respectively. It is found that the presence of moisture has almost no influence on the UV–vis spectra of the melt, while it generally contributes to further decrease M_n. This implies that the degradation mechanism under moisture is different from that of the dry PLLA. For details see next section. It is noteworthy that at a throughput of 0.2 kg/h and higher screw speed, moisture even does not have significant influence on M_n. The possible reason is that lower throughput and higher screw speed yields higher SME, which results, via increasing of melt temperature, in more efficient evaporation of moisture during the extrusion. For instance, for the moist PLLA being processed at throughputs of 0.2 and 0.61 kg/h with screw speed of 300 rpm, the SME values are 20 and 11 kJ/g, respectively.

3.3. Mechanisms of thermal degradation

Thermal degradation of PLA is very complex and various mechanisms have been postulated, including (a) intramolecular transesterification; (b) intermolecular transesterification; (c) hydrolysis; and (d) pyrolitic elimination [28–34]. The UV–vis data in the present study show that minimum absorption occurs at the processing condition of 180 °C, 0.34 kg/h and

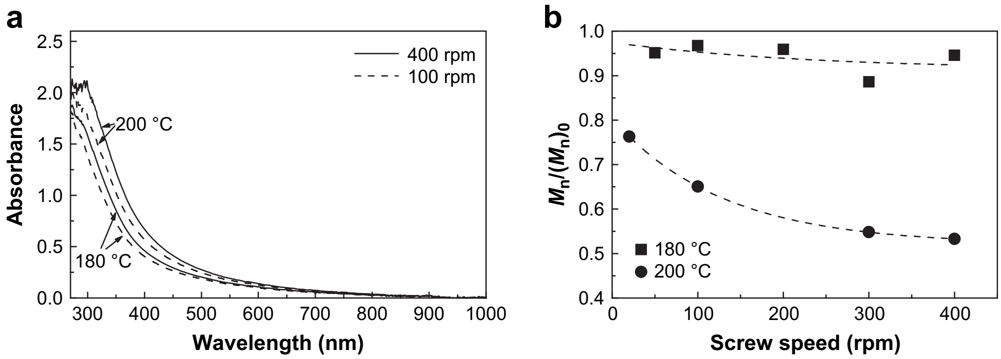

Fig. 5. Influence of extrusion temperature on the UV–vis spectra (a) and the normalized molar mass of PLLA (b) at different screw speeds. The throughput was kept constant at 0.34 kg/h. The dotted lines in (b) are guides for the eyes.

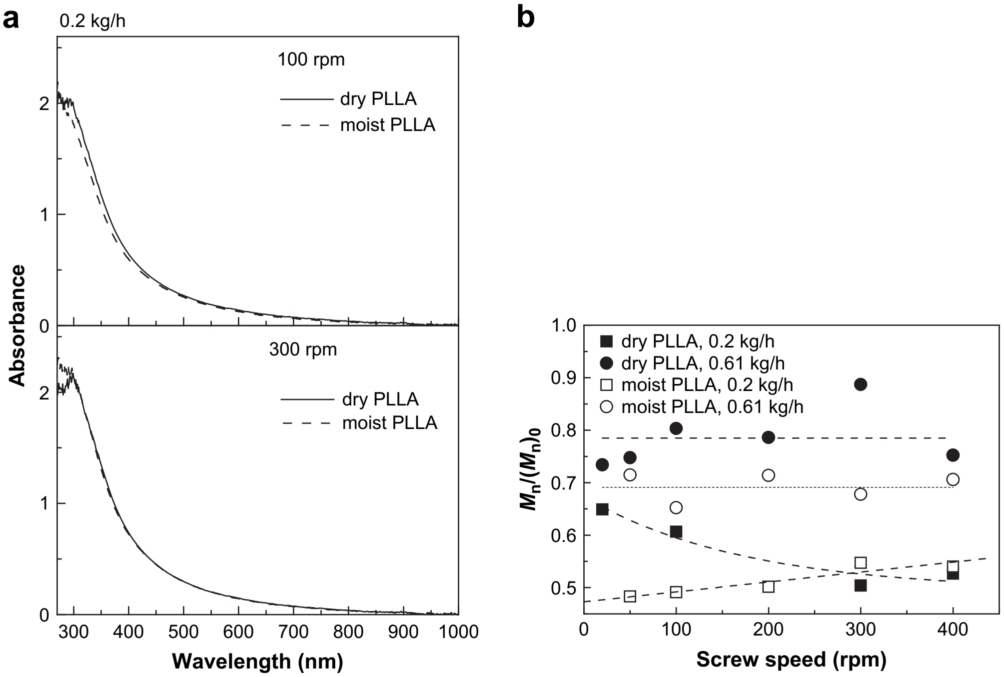

Fig. 6. Influence of moisture on the UV–vis spectra (a) of PLLA melt at 200 °C, and the normalized molar mass (b). The dotted lines are guide for the eyes.

50 rpm, corresponding to minimum process induced degradation. It is also evident that the UV–vis spectra become stronger in intensity and apparently shift to higher wavelength with increasing processing temperature and screw speed, and with decreasing throughput. It is known that the absorption maximum of a polymer is shifted to higher wavelengths when the number of conjugated double bonds increases [20,35]. Therefore, the red-shift of the spectra in the present work might be ascribed to the formation of conjugated double bonds by thermal degradation. A scheme of the pyrolytic elimination of poly(lactic acid) is shown in Fig. 7 [31]. It can be seen that the pyrolytic elimination results in species containing conjugated double bonds due to the carbonyl group. Therefore, the assumption of pyrolytic elimination is supported by the UV–vis spectra.

As shown previously, the presence of moisture in PLLA has almost no influence on the spectra of the melt, while generally contributes to further decrease in M_n. The possible reason is that additional hydrolytic degradation occurs in moist PLLA during processing. Hydrolysis, however, only reduces molar mass but does not contribute to increasing UV–vis absorption, since no conjugated double bonds are formed. The hydrolysis scheme of poly(lactic acid) [31] is shown in Fig. 8.

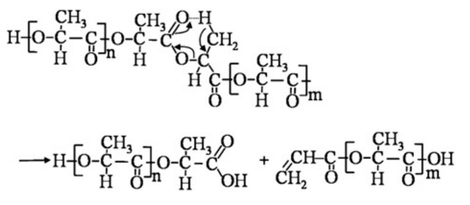

Fig. 7. Scheme of the pyrolytic elimination of poly(lactic acid).

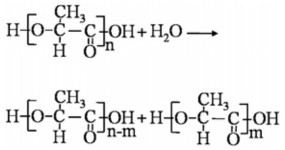

Fig. 8. Scheme of the hydrolysis of poly(lactic acid).

3.4. Correlation of the spectral contribution of the degradation products with M_n and SME

It has been reported that poly(lactic acid) itself exhibits a maximum UV absorption at 240 nm in chloroform due to the ester group in the polymer [16]. If we assume that the thermal degradation of PLLA could be ignored when being processed at 180 °C, 0.34 kg/h and 50 rpm, the corresponding absorption spectrum can be taken as reference spectrum. After subtracting that reference spectrum from all the UV–vis spectra discussed in Section 3.1, difference spectra (ΔA) are obtained. The difference spectra exhibit a maximum at wavelength of about 310 nm for all processing conditions, indicating the wavelength range of the most significant spectral changes due to degradation. Therefore the ΔA curves mirror the net contribution of the new chromophoric groups formed by the thermal degradation. An example is shown in Fig. 9. For correlation of processing conditions and molar mass we have chosen the absorption difference ΔA at $\lambda = 310$ nm as an operational parameter. It is found that ΔA increases, in the wavelength region at about 310 nm with increasing processing temperature and screw speed as well as with decreasing throughput (not shown). This means that increase in ΔA (310 nm) is accompanied by decrease in M_n, and increase in SME.

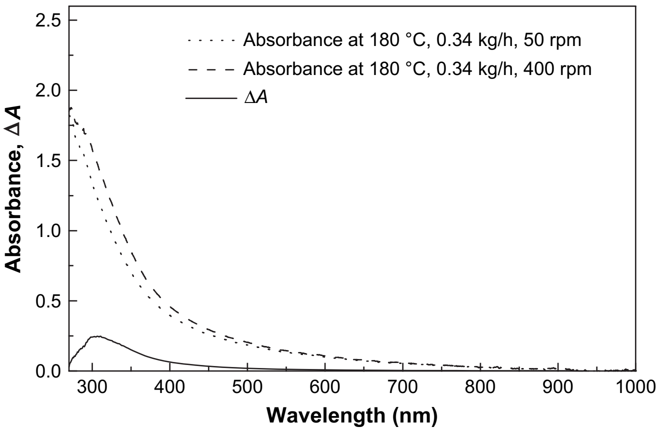

Fig. 9. UV–vis spectra of PLLA melt at indicated conditions and their difference spectrum (ΔA).

The data of ΔA (310 nm) against M_n are plotted in Fig. 10. The data for dry PLLA can be described by an empirical linear relationship:

$$\Delta A(310\,\text{nm}) = 1.48 - \left(1.14 \times 10^{-6}\right) \times M_n \qquad (2)$$

The standard errors are 0.26 for the intercept and 0.28×10^{-6} for the slope. This relationship indicates that UV–vis absorption of the melt therefore can be used to get an estimate of the molar mass of the extrudates of dry PLLA, regardless of variations in extrusion parameters. For comparative purpose, the data of moist PLLA (solid symbols) were also included into Fig. 10. The data of moist PLLA apparently deviate from the fitting line of the data of dried PLLA. This most likely can be explained by the additional hydrolytic degradation occurring during processing, as already discussed above. The hydrolysis only results in reduced molar mass but does not contribute to increase of UV–vis absorption (see scheme for hydrolysis in Fig. 8).

The data of ΔA (310 nm) against SME for dry PLLA are plotted in Fig. 11. It is found that the SME dependence of ΔA (310 nm) is a function of processing temperature. The influence of SME on ΔA (310 nm) is more pronounced at 200 °C than at 180 °C. Since the SME is proportional to the screw speed (Eq. (1)), the trend shown in Fig. 11 agrees well with the observation in Fig. 5b, where the influence of screw speed on the degradation is also more pronounced at 200 °C than at 180 °C. An explanation already has been given in the context of Fig. 5b. From Fig. 11, it can also be concluded that the parameter SME alone is not suitable for estimating the molecular mass reduction of PLLA, since the SME dependence of ΔA (310 nm) depends significantly on the barrel temperature. This is completely different to the behavior of starch, where a semi-logarithmic dependence of the molar mass values on SME, regardless of extruder type or processing conditions, was reported [26].

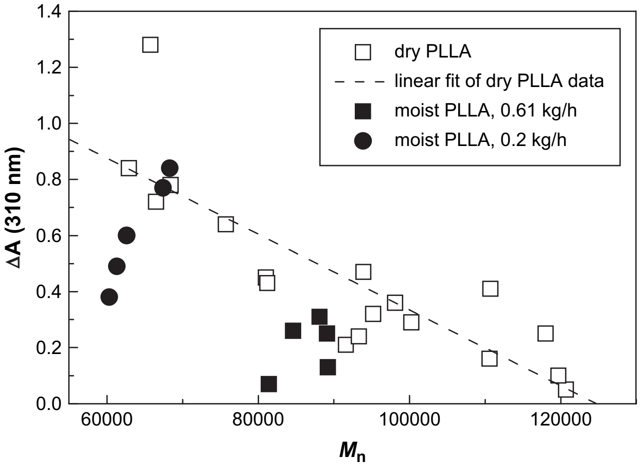

Fig. 10. Relationship between ΔA (310 nm) and M_n.

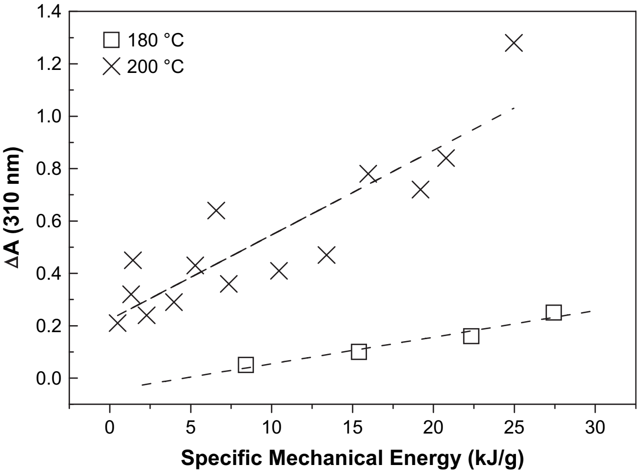

Fig. 11. Plot of ΔA (310 nm) *versus* SME at indicated temperatures for dry PLLA (the dotted lines are guides for the eyes).

3.5. In vitro biodegradation

To evaluate the effects of processing parameters of PLLA on the biodegradation rate of the extrudates, an *in vitro* biodegradation experiment was also performed for selected extrudates. It has been reported that the biodegradation rate of high molar mass PLLA at 37 °C is very low. It takes a span of 5 years or more until degradation has completed (i.e. the sample has dissolved completely) [36–38]. *In vitro* experimentation at elevated temperatures can accelerate the degradation process while causing no change in the hydrolysis mechanism, allowing direct comparison of the degradation rate of various polymers [36,39,40]. In this study, the degradation of PLLA was performed at 60 °C. The selected extrudates correspond to processing conditions of 180 °C, 0.34 kg/h, and 50 or 400 rpm, respectively. The UV–vis spectra and normalized molar mass of the materials can be found in Fig. 5a and b. The *in vitro* weight loss as function of time for the extrudates is shown in Fig. 12. It is found that higher *in vitro* weight loss is related to higher UV–vis absorption of the extruded materials. Since higher UV–vis absorption for dry samples is correlated with lower molar mass of the extruded materials, the results obtained here on PLLA are generally consistent with literature. This

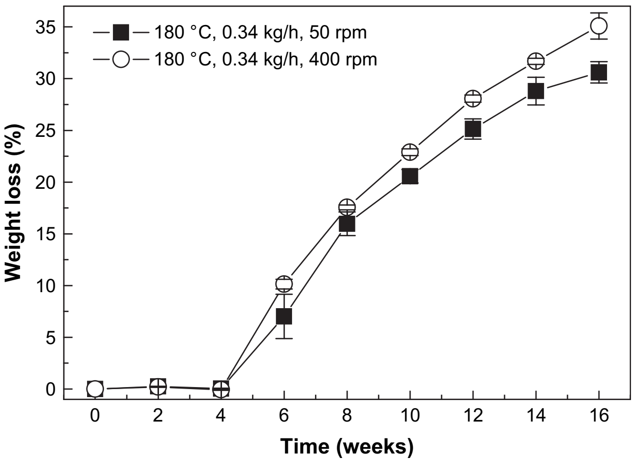

Fig. 12. *In vitro* weight loss as function of time for the materials extruded at the indicated conditions.

means, the larger the initial molar mass of a bio-absorbable polymer the longer the biodegradation time [14,41].

4. Conclusions

It can be stated that UV–vis spectroscopy technique provides a powerful and non-destructive tool for real time detection of the thermal degradation of PLLA which can be used to optimize the processing conditions. UV–vis spectroscopy is very sensitive to minute colour changes of the PLLA melt.

A clear correlation exists between increasing UV–vis absorption of the melt and decrease of the molar mass of the extrudates, where the latter is a measure for the degradation. After subtracting a reference UV–vis spectrum (corresponding to PLLA melt without degradation) difference spectra corresponding to new chromophoric groups yielded by thermal degradation were obtained.

For dry PLLA there is a linear relationship between the absorption of the difference spectra and the molar mass, independent on the extrusion conditions.

The molar mass reduction during processing was found to be caused mainly by thermal degradation. The corresponding heat input is due to direct heating and conversion of mechanical energy. The latter is related to screw speed and torque. An other important factor for thermal degradation is the residence time.

The presence of moisture in the polymer does not significantly influence the UV–vis spectra of the melt but contributes to further molar mass reduction of the extrudates. Pyrolytic elimination will be the main degradation mechanism for dry PLLA and will be responsible for the colour formation and molecular weight reduction, while an additional hydrolysis mechanism in moist PLLA only reduces molar mass but does not contribute to increasing UV–vis absorption.

In vitro biodegradation experiments show that the processing parameters have a detectable influence on the biodegradation behavior of the PLLA extrudates. The *in vitro* biodegradation rate corresponds well with the intensity of the UV–vis absorption.

Besides the application in monitoring the extrusion of PLLA, the UV–vis method will also be suitable for optimizing product quality and processing of other biodegradable polymers during extrusion. Furthermore, the method can be extended to monitor degradation of traditional polymer materials and other processing techniques.

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