Available online at www.sciencedirect.com

ScienceDirect

Polymer Degradation and Stability 93 (2008) 925–931

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

Polylactide compositions. The influence of ageing on the structure, thermal and viscoelastic properties of PLA/calcium sulfate composites

Miroslaw Pluta [a,*], Marius Murariu [b], Michaël Alexandre [b],
Andrzej Galeski [a], Philippe Dubois [b,c]

[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
[b] Materia Nova asbl, Parc Initialis, Avenue Nicolas Copernic 1, B-7000 Mons, Belgium
[c] Centre of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials (LPCM),
University of Mons-Hainaut, Académie Universitaire Wallonie-Bruxelles, Place du Parc 20, B-7000 Mons, Belgium

Received 10 December 2007; received in revised form 25 January 2008; accepted 3 February 2008
Available online 10 February 2008

Abstract

High-performance composites prepared by melt-blending polylactide (PLA, L/D isomer ratio of 96/4) with various amounts of β-anhydrite II (AII), the dehydrated form of calcium sulfate hemihydrate obtained by a specific thermal treatment at 500 °C, have been aged to study the evolution of their physical and mechanical properties with time. The effect of 1-year ageing under ambient conditions (below T_g of PLA) for selected composites, i.e., filled with 20 and 40 wt% AII, was determined and compared to unfilled PLA with the same processing and ageing history. Samples with an initial amorphous PLA matrix, obtained by fast quenching from the melt, were characterized before and during ageing. The changes in physical parameters have been studied using dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and density measurements. Surprisingly, for all the samples, an increase of the storage modulus (E') was recorded, as a result of ageing. This improvement was ascribed to the reorganization of the PLA structure induced by ageing. The structural reorganization was also reflected by a slight increase of PLA density and changes in thermal behaviour. The X-ray investigations showed unchanged crystallographic structure of AII both during blending with molten PLA and in the composite systems after ageing. The surprising stability of the thermo-mechanical properties of PLA and PLA/AII composites is in agreement with the results of size exclusion chromatography analysis (SEC) which did not show significant changes of PLA molecular weights brought out by ageing.

Keywords: Polylactide; Calcium sulfate; Composite; Mechanical properties; Ageing

---

1. Introduction

The market for biodegradable materials is growing every year and important increases are expected for those applications in which the biodegradability offers clear advantages for customers and the environment, with typical examples such as packaging, compost bags, agricultural films, coatings and textiles [1,2]. As far as the polymer matrix is concerned, the aliphatic polyesters and more particularly poly(lactic acid) (PLA) hold a key position. PLA seems to be one of the most promising candidates for future developments; it is not only biodegradable but also produced from annually renewable resources, like beet sugar or corn starch [3–8]. Because PLA has been recently considered as an alternative in replacing petrochemical polymers, there is a strong demand to extend the range of PLA properties. On the other hand, for many applications, PLA remains more expensive than the fossil fuel derived plastics and in this context the price/performance aspects can represent a main marketing argument for the use of new PLA grades.

As is well-known, a sizeable proportion of all thermoplastics worldwide are compounded and/or reinforced with fillers or fibres. Their function is to improve final product specific

---

* Corresponding author. Department of Polymer Physics, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland. Tel.: +48 42 6803237; fax: +48 42 6847126.
E-mail address: mpluta@bilbo.cbmm.lodz.pl (M. Pluta).

0141-3910/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2008.02.001

properties and/or to reduce costs. Similarly, for further applications, the profile of PLA properties can be modified by combining the polyester matrix with various dispersed phases: fillers or reinforcements, (nano)additives or other polymers. The mineral-filled compositions based on PLA have been firstly used in limited quantities for biomedical applications taking the advantage of PLA biodegradability and biocompatibility. In this frame, typical mineral fillers combined with PLA were hydroxyapatite, calcium carbonate, calcium phosphate, etc. [9–14]. For some industrial applications, the use of PLA with mineral fillers, either surface modified or not, can be an interesting solution to reduce its global cost and to improve some specific properties such as rigidity, heat deflection temperature, processability, isotropic shrinkage, etc.

In this context, in response to the demand for extending PLA applications range while reducing its production cost, it has been recently demonstrated by some of us [15] that commercially available PLA can be effectively melt-blended with previously dehydrated gypsum (anhydrite II form or AII), actually a by-product of lactic acid production. These two products from the same source as origin can lead by melt-mixing to polymer composites characterized by remarkable thermal and mechanical performances [15,16] and improved barrier properties to water vapour [17]. The physical properties as well as the dispersion of the filler into PLA matrix and the phase structure features of the un-aged composites have been characterized in detail in our previous work [15,16].

Since the prepared composites are potentially interesting as biodegradable hard packaging or for technical applications, it is important, for further use, to have information concerning their stability or modification during ageing. Accordingly, this study mainly focusses on characterization of the influence of ageing up to 1 year (under ambient conditions) on the physical properties of PLA/AII composites and for comparison, of unfilled PLA. This paper reports the most relevant modifications induced by ageing for the considered systems as evidenced by viscoelastic measurements (DMTA), calorimetric characterization (DSC) and XRD analyses. The molecular characteristics of the PLA, before and after ageing, were evaluated by size exclusion chromatography (SEC), whereas the change of PLA density was determined by a conventional technique. Finally, the stability of the crystallographic structure of AII was investigated using X-ray diffraction technique and selected aspects in relation to the filler stability during processing and in composites after ageing are discussed and correlated with respect to their potential fabrication and use.

2. Experimental

2.1. Materials

Polylactide (PLA, number average molar mass = 74,500 g/mol, residual monomer content = 0.18%, L/D isomer ratio of 96/4, MFI (190 °C, 2.16 kg) = 6.6 g/10 min) was supplied by Galactic s.a. under the tradename Galastic, and dried 4 h at 110 °C under vacuum just before use. The drying conditions used enable reduction of moisture below 250 ppm, which is essential to minimize PLA hydrolysis during melt-processing.

Calcium sulfate hemihydrate – β form ($CaSO_4 \cdot 0.5H_2O$), a by-product from the lactic acid production process with mean particle diameter of 9 μm was provided by Galactic s.a. and dried (see below) just before the melt-mixing with PLA.

2.2. Preparation

β-Anhydrite II (AII) was obtained by dehydration of calcium sulfate hemihydrate in a Nabertherm 3 L furnace at 500 °C for 1 h. PLA/AII composites were prepared by melt-compounding at 190 °C using a Brabender bench scale kneader equipped with cam blades (for 3 min at 30 rpm, followed by 3 min at 60 rpm). PLA alone was also melt-processed under the same conditions to have a reference material. Samples (1 mm) were prepared by compression moulding (at 190 °C) followed by a rapid cooling from the melt between metal blocks at low temperature (∼ 0 °C) to produce a PLA matrix quenched into the amorphous state. Then, the samples were stored under normal (atmospheric) conditions for 1 year to allow ageing. The composition of the samples considered in this study, before and after ageing, as well their codification is given in Table 1.

2.3. Characterization

Molecular weight parameters (number average molar mass (M_n), and polydispersity index (M_w/M_n)), of PLA samples (unaged and aged) were determined by size exclusion chromatography (SEC) using the procedure described in Ref. [15]. SEC analysis allows determining the effect of melt-compounding and of ageing on molecular characteristics of PLA in relation to the sample composition.

The changes of density during ageing of the unfilled PLA were measured in solution of distilled water and zinc chloride using a flotation method [18]. The solution temperature was controlled to a constant 23 °C. The composites were not investigated by this method due to sorption ability that is typical for dehydrated fillers.

The thermal properties of the samples were investigated using a DSC 2920 (TA Instruments) under nitrogen atmosphere from 0 to 180 °C using a heating ramp of 3 °C/min.

XRD characterization of AII powder and composite systems (before and after ageing) was performed at room temperature using a Siemens D5000 diffractometer with the Cu Kα

Table 1
Specification of considered samples

History	Filler		
	0%	20%	40%
	Codification of samples and AII content (wt%)		
Un-aged	PLA	PLA20AII	PLA40AII
1-year aged	agPLA	agPLA20AII	agPLA40AII

radiation ($\lambda = 1.5406$ Å) in reflection mode for 2θ angle varying from 10 to 60° by step of 0.04° and scanning rate of 2°/min.

Viscoelastic properties of the un-aged and aged samples were measured using MkIII DMTA apparatus (Rheometric Scientific, Inc.) in a dual-cantilever bending mode. Samples in the form of strips ($27 \times 10 \times 1$ mm) were investigated. The dynamic storage and loss moduli (E' and E'', respectively) were determined at a constant frequency of 1 Hz as a function of temperature from −100 to 145 °C at a heating rate of 2 °C/min, for a sinusoidal deformation of ±0.32 μm amplitude.

3. Results and discussion

3.1. SEC characterization of PLA

Because the risk of hydrolytic degradation of PLA is extremely important during manufacturing, storage and end-use of PLA/AII products, the molecular characteristics (number average molar mass, M_n and polydispersity index, PI) were determined for unfilled PLA and for PLA extracted from the composite samples, before and after ageing (Table 2).

As revealed by data shown in Table 2, the melt-processing of PLA alone or in the presence of the filler (40 wt% AII) leads to a decrease of approx. 15% in M_n and generally, to slight increase of polydispersity index (PI) with respect to the unprocessed PLA. These changes of molecular characteristics of the melt-processed PLA were expected due to the well-known sensitivity of polylactide to thermo-mechanical degradation at high temperature under mechanical shear [19,20]. Furthermore, the ageing of the unfilled PLA does not significantly change the molecular parameters (M_n and PI) of the material as the parameters determined are essentially comparable within the experimental accuracy of ±10%.

On the other hand, the ageing of PLA40AII up to 6 months, has no noticeable effect on modification of molecular characteristics and in this context the stability of the principal properties of this composite can be expected. Moreover, it is important to emphasise that the molecular masses of unfilled PLA seem unaffected by ageing after 1 year and even after more than 2 years ($M_n = 63{,}000$, PI = 2.1), while the composite experiences a slight reduction of M_n and a significant broadening of the polydispersity index ($M_n = 55{,}000$, PI = 2.4), suggesting the beginning of the hydrolytic degradation of the PLA matrix.

Table 2
PLA molecular weights and polydispersity indices (PI = M_w/M_n) for un-aged and aged samples (SEC analysis accuracy: 10%)

Sample history		Sample			
		PLA[a]		PLA40AII	
		M_n	PI	M_n	PI
Un-aged		64,000	2.2	63,000	2.2
Aged	3 Months	62,000	2.0	67,000	1.9
	6 Months	64,000	2.1	65,000	2.2
	>1 Year	63,000	2.1	55,000	2.4

[a] PLA before processing: $M_n = 74{,}500$, $M_w/M_n = 2.0$.

In conclusion, the SEC characterization indicates that the PLA and PLA/AII composites are characterized by relatively good stability during heating treatment (melt-blending) and during ageing at ambient temperature for at least 6 months.

3.2. Thermal behaviour

Fig. 1 shows DSC heating thermograms for 1-year aged (thick line) and un-aged samples (thin line) as reference. Since the thermal behaviour of the un-aged samples has been described in detail in our previous paper [16], the discussion of calorimetric results in this study is mainly focused on the influence of ageing on the thermal properties of PLA/AII composites.

Both un-aged and aged samples show similar thermal transitions on heating: glass–rubber transition (T_g), cold crystallization with peak (at T_c) and finally, a bimodal melting process at higher temperature (T_{m1} and T_{m2}). The thermal events for the aged samples are, however, much more pronounced than for the un-aged counterparts, particularly at T_g and T_c regions. In contrast to the initial samples, the aged ones show distinct endothermic peak following the T_g and sharper cold crystallization (exotherm) with peak localized at a lower temperature.

In addition, the melting behaviour of aged samples, particularly for composites, is also modified and the first melting (enthalpic) component (at T_{m1}) is smaller than the second one (at T_{m2}). An opposite relation concerning the magnitude of these melting components is observed for the un-aged composites. It is believed that for the aged samples the increase of the melting contribution at T_{m2} can be correlated with the decrease by ageing of the cold crystallization temperatures (T_c). Indeed, when cold crystallization occurs at lower T_c, less perfect crystallites are formed and they are able to recrystallise during DSC heating scan (such a recrystallisation event can be compensated by concomitant melting and is, therefore,

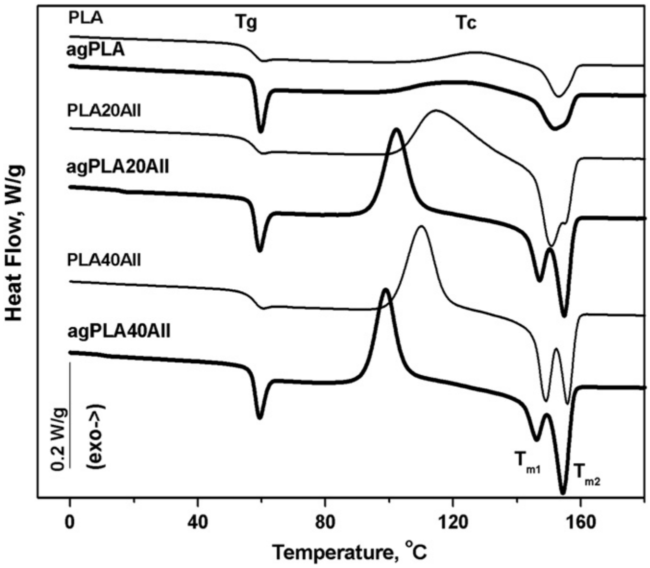

Fig. 1. DSC thermograms of aged samples (agPLA, agPLA20AII and agPLA40AII) − thick curves and un-aged samples (PLA, PLA20AII and PLA40AII) − thin curves, recorded using a heating ramp of 3 °C/min.

not revealed on a conventional DSC curve). Consequently, the crystallites formed (recrystallised) at higher temperature are more stable and have higher contribution on the melting process observed at T_{m2}.

Table 3 presents the calorimetric parameters characterizing the following processes: glass transition (at T_g) with accompanied relaxation enthalpy (ΔH_r), cold crystallization process (T_c and ΔH_c) and melting processes (T_{m1}, T_{m2} and ΔH_{m1}, ΔH_{m2}).

By analyzing the results of DSC measurements for the unfilled PLA and PLA/AII composites (see Table 3) it could be pointed out that the T_g values are not significantly affected either by the ageing process or by the presence of AII. However, the relaxation enthalpy ΔH_r (following the T_g) is considerably higher for the aged samples than for un-aged counterparts. For un-aged samples, it decreases with the increase of AII content from 1.6 for the unfilled PLA to 1.1 J/g for PLA40AII, while for the aged counterparts a decrease from 5.6 to 4.8 J/g was recorded, respectively. This decrease of the ΔH_r with the AII content can suggest confinement of some fraction of PLA chains in the interphase (at the filler surface) which, therefore, cannot contribute to the ΔH_r. On the other hand, the T_c decreases in correlation with the percentage of filler, from 127 to 110 °C for the un-aged samples, and after ageing, from 122 to 99 °C. At the same time ΔH_c increases with the AII content for the un-aged samples (from 8.2 to 27.1 J/g) and this increase is slightly higher for the aged samples (from 9.1 to 29.3 J/g, with some exception for agPLA40AII). The increase of the crystallization ability after ageing can be attributed to formation of additional nuclei as a result of ageing and reorganization of the PLA structure.

In the region of melting temperatures – in direct correlation with the filler percentage, the melting process becomes more complex and double melting peaks are recorded, with domination of that one at T_{m2} for the aged composites. This reflects a different thermal stability of the crystallites formed in the samples characterized by different composition and ageing history. For each sample, however, the values for melting enthalpy are close to the cold crystallization enthalpy. This confirms that the PLA matrices were characterized by an essentially amorphous structure. However, this structure is unstable, it underwent some physical reorganizations during ageing as reflected e.g., by the changes in the thermal behaviour of aged samples in comparison to those of un-aged samples. In explanation of that it should be accounted that in the starting melt-quenched PLA a non-equilibrium glassy state was achieved. This state evolves upon ageing towards a more stable state via molecular rearrangements. The structural reorganization induced in amorphous PLA by ageing can be further confirmed by changes in intensity of an amorphous halo of X-ray diffraction spectrum [21]. In the case of unfilled PLA this rearrangement is associated with a small increase in density, from 1.251 g/cm^3 for the starting sample, to 1.255 g/cm^3 after 1-year ageing (after 3-month ageing the PLA density increased to 1.253 g/cm^3, the density of a single crystal of PLA was reported to be 1.290 g/cm^3 [20]).

On the other hand, it is essential to emphasise that the effects of the physical ageing are dependent not only on the time of ageing, but also on other parameters such as temperature, initial crystallinity and thermal history, PLA molecular weights and composition, etc. as other studies have been described in detail elsewhere [22–24]. In conclusion, the thermal behaviour – particularly the glass transition relaxation effect and crystallization ability of the PLA component from the glassy, amorphous state are affected by both the sample composition and ageing process. The presence of AII filler in the PLA matrix provides additional nuclei for cold crystallization and their number further increases in the aged samples due to the physical reorganization of the amorphous PLA material.

3.3. Viscoelastic properties

The effect of ageing on the unfilled PLA and PLA/AII composites was also investigated in isochronal measurements of viscoelastic properties as a function of temperature using DMTA. Fig. 2a–c shows in comparison the storage modulus (E') and loss modulus (E'') spectra for the aged and un-aged samples (thick and thin lines, respectively).

Since the viscoelastic properties of the un-aged samples have been already described in a previous study [16], this work is mainly focused on the most relevant changes in the behaviour of the E' and E'' brought out by ageing. As far as the composites are concerned, E' increases with the AII content as expected but, more surprisingly, it also increases with the

Table 3
Comparison of calorimetric data of un-aged and 1-year aged PLA samples as determined from conventional DSC heating thermograms (ramp of 3 °C/min)

Sample	Glass transition		Cold crystallization		Melting		
	T_g (°C)	ΔH_r (J/g)	T_c (°C)	ΔH_c (J/g)	T_{m1}; T_{m2} (°C)	ΔH_{m1}; ΔH_{m2} (J/g)	ΔH_T (J/g)
PLA	57.8	1.6	127	8.2	153	8.4	8.4
agPLA	57.6	5.6	122	9.1	152	11.8	11.8
PLA20AII	58.1	1.3	116	24.2	151; 153	17.0; 7.5	24.5
agPLA20AII	58.1	5.4	102	29.3	147; 155	14.9; 15.5	30.4
PLA40AII	58.1	1.1	110	27.1	149; 156	16.8; 11.5	28.3
agPLA40AII	58.1	4.8	99	25.0	146; 154	12.6; 15.8	28.4

Observation: enthalpy (ΔH) values are related to the mass unit of PLA.

Abbreviations: T_g – glass transition temperature determined from the inflection point of the heat flow curve, ΔH_r – excess enthalpy relaxation following the glass transition (the value is determined from the peak area using a sigmoid baseline), T_c, ΔH_c – temperature of the cold crystallization peak and corresponding crystallization enthalpy, T_{m1}, T_{m2} and ΔH_{m1}, ΔH_{m2} – temperature of the melting peaks and corresponding melting enthalpies, ΔH_T – total melting enthalpy.

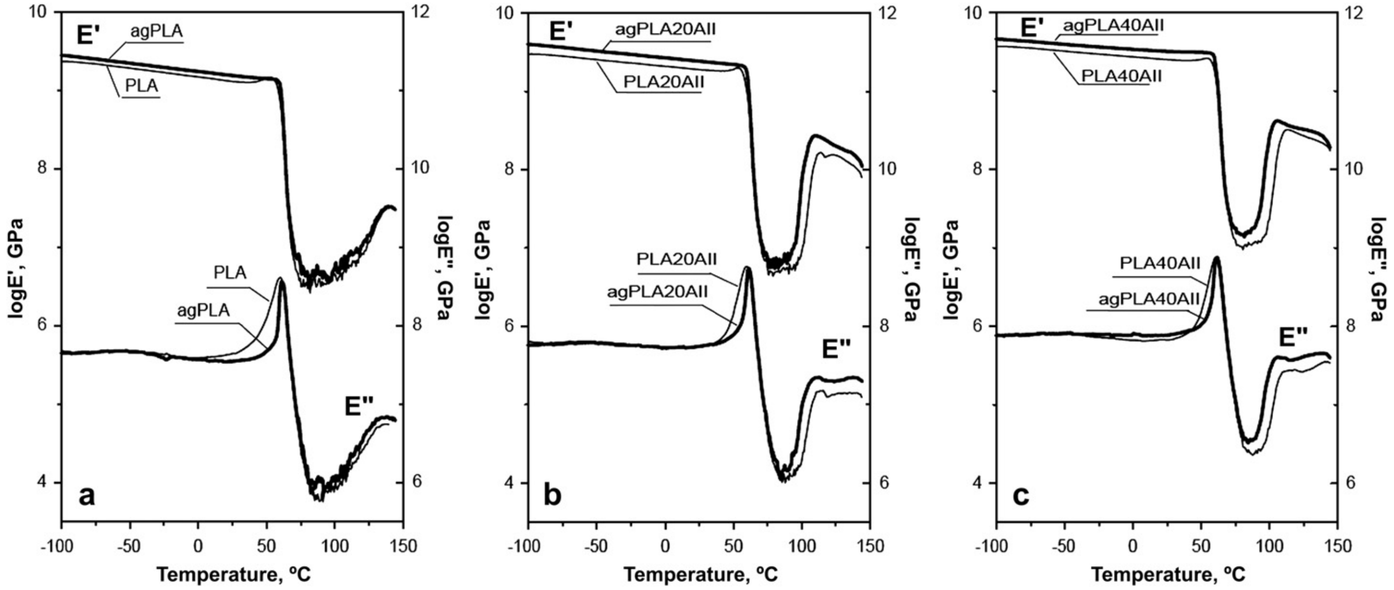

Fig. 2. (a–c) Comparison of E' and E'' spectra of aged (thick line) and un-aged samples (thin line).

ageing of PLA and PLA/AII samples. For example, the increase of E' at 25 °C is 19% for agPLA (1.3 GPa for un-aged PLA), 29% for agPLA20AII (1.8 GPa for un-aged PLA20AII) and 27% for agPLA40AII (2.5 GPa for un-aged PLA40AII). The increase of E' with ageing reflects the increase of rigidity that can be connected to the increase of density induced by ageing as discussed above.

Interestingly, the ageing also modifies the viscoelastic behaviour in the T_g region. After ageing, the small E' peak before the glass–rubber transition disappears (it is ascribed to the relaxation of internal stresses frozen in the polymer during sample preparation *via* melt-quenching [16]), and a low temperature shoulder of the E'' peak decreases. These changes are related with higher density (better "packing") of the amorphous material revealed in the aged samples.

In order to characterise quantitatively the changes of the mechanical loss at the T_g region connected with the sample composition and ageing process, the temperature of the E'' peak was determined (i.e., T_g from mechanical loss) together with the following parameters: the E'' peak area (A), its half-width ($W_{1/2}$) and its height (H). These parameters (with the exception of T_g) were related to the respective parameters of the unfilled and un-aged PLA sample as reference. The parameters obtained A_{rel}, $W_{1/2rel}$ and H_{rel}, as well as T_g are shown in Table 4 (The estimation was performed in the temperature region from 25 to 80 °C and a linear E'' scale was used).

Firstly, from Table 4 it is seen that the T_g determined from the DMTA is sensitive to the composition and ageing history of the samples as its value tends to increase with ageing and filling (T_g from the DSC data appeared to be less sensitive – Table 3). For the un-aged samples, the mechanical loss intensity systematically increases with the filler content. For example, the E'' peak area (A_{rel}) and its height (H_{rel}) are increased by 73 and 85%, respectively, at 40 wt% of AII. This increase of the E'' peak with the filler content can be attributed mainly to the contribution of the mechanical loss generated in the interface regions. In turn, the aged samples also exhibit the increase of E'' peak with the filler content, however, the magnitude of the mechanical loss is distinctly smaller than for the un-aged and unfilled PLA reference (and for un-aged counterpart as well). For example, for the agPLA: $A_{rel} = 58\%$, $H_{rel} = 88\%$ and $W_{1/2rel} = 48\%$ with respect to the values determined for the un-aged and unfilled PLA reference. The diminution of the mechanical loss at E'' peak intensity after ageing reflects the decrease of the mechanical energy dissipation in the structure reorganized during ageing.

At higher temperatures coinciding with the cold crystallization, the increase of E' and E'' observed for the aged samples is higher and occurs in a lower temperature range than for the un-aged counterparts. These results can be directly related to DSC observations and show that DMTA is fairly sensitive to the crystallization processes. Summarizing, ageing of the considered samples increases their rigidity and chain packing that implies lower ability for dissipation of mechanical energy through molecular motion. Similar relations concerning the "physical ageing" below T_g for unfilled PLA – i.e., the increase of E' were reported by Celli and Scandola [22]. Moreover, the increase of E' of the PLA/AII samples after ageing can also suggest stable interphase properties for PLA/AII

Table 4
Parameters characterizing the mechanical loss in the glass transition region of the un-aged and aged samples with different compositions

Sample	T_g (°C)	A_{rel} (%)	$W_{1/2\ rel}$(%)	H_{rel} (%)
PLA	59.8	100	100	100
PLA20AII	59.5	132	95	140
PLA40AII	60.5	173	92	185
agPLA	60.7	58	48	88
agPLA20AII	61.5	91	51	134
agPLA40AII	61.7	133	53	177

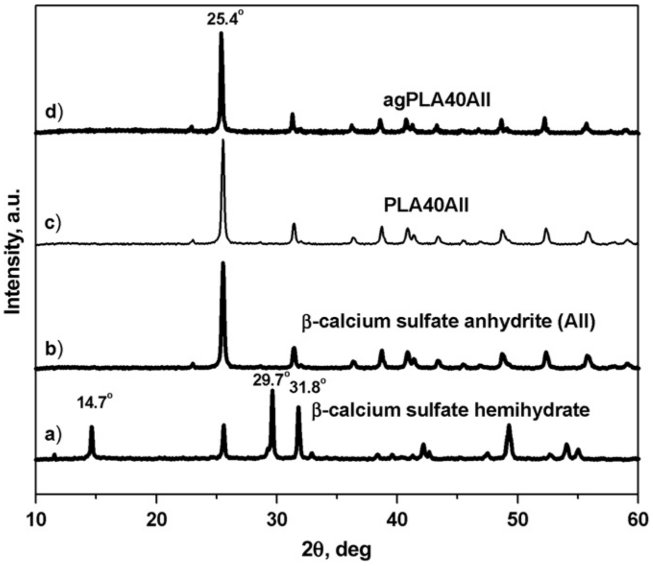

Fig. 3. Diffractograms of starting β-calcium sulfate hemihydrate powder (a), of β-calcium sulfate anhydrite II (b), of PLA40AII composite un-aged (c) and 1-year aged (d).

composites, a favourable conclusion in the perspective of use of these materials in technical applications.

3.4. X-ray investigation

The crystal transformations of calcium sulfate and its various hydrated and dehydrated forms are considered in detail elsewhere [25–28]. For this study the crystalline organization of the β-calcium sulfate hemihydrate and anhydrite II form, was detected by XRD. The diffractogram of β-calcium sulfate hemihydrate powder (i.e., $CaSO_4 \cdot 0.5H_2O$ as received) is shown in Fig. 3 – curve a. It is featured by several intense peaks at $2\theta \approx 14.7$, 25.4, 29.7 and 49.2°. After dehydration, as exemplified by the diffractogram presented in Fig. 3 – curve (b), the crystalline structure of obtained β-calcium sulfate anhydrite ($CaSO_4$) is different. It is characterized by only one intense peak at $2\theta \approx 25.4°$ and a number of smaller ones at higher scattering angles.

This crystallographic form is preserved during blending with the molten PLA and, moreover, it is also stable in composites because similar diffractograms have been recorded after ageing (compare curves b, c and d). When embedded in the PLA matrix, AII is sufficiently stable not to re-form the hemihydrate form after 1-year ageing. These results allow an important key conclusion that the AII used as filler in PLA (and presumably in other polymers) is attractive from the view-point of the structural stability and further, for the possibility of technological recycling of PLA/AII composites (no detrimental sequestration of water by anhydrite re-hydration upon ageing).

4. Conclusions

PLA composites filled with calcium sulfate, i.e., β-anhydrite II form (AII), were prepared by conventional melt-blending. Since these PLA/AII composites are potentially interesting for further applications, the effect of 1-year ageing under normal (atmospheric) conditions has been studied in relation to the filler content (20 and 40 wt%) and compared to the unfilled PLA with the same thermal history, i.e., characterized by an amorphous structure. In summary, the study of the molecular, thermal and viscoelastic properties showed that the performances of the PLA/AII composites are maintained after ageing. The measured mechanical properties (E' modulus) were even enhanced by ageing process. This modification was ascribed to the increase of local order in the amorphous phase of PLA. The structural reorganization of PLA material was shown by DSC investigations, particularly at the T_g region (in accordance with the E'' response) and by a small increase in density. At the same time, the structural stability of the AII was confirmed using the X-ray method which proved the filler stability towards hydration in the composite systems with amorphous PLA matrix. Finally, it has been shown that the molecular weights of the aged PLA – from unfilled PLA and composites did not decrease upon ageing, at least after 6 months, typical period for a potential application such as packaging.

Acknowledgments

The authors thank Galactic s.a., the ‘Région Wallonne’ and European Community for financial support in the frame of INTERREG III: MABIOLAC – “Production of biodegradable composite materials based on lactic acid”. LPCM and Materia Nova are grateful for the financial support from the ‘Région Wallonne’ and European Community (FSE, FEDER) in the frame of Objectif-1 and Phasing Out: Materia Nova. This work was also partially supported by the Interuniversity Attraction Poles Programme – Belgian State – Belgian Science Policy (PAI-6/27). M.P. and A.G. thank also CMMS PAS Poland for the support of this research. The authors thank Amália Da Silva Ferreira for assistance in preparation of the composites.

References

[1] Platt D. Biodegradable polymers – market report. Smithers Rapra Limited; 2006.
[2] Johanson D. Renewable raw materials, DG Entreprise/E1-report. 2001.
[3] Mochizuki M, Tsuji H. Properties and applications of aliphatic polyester products. In: Doi Y, Steinbüchel A, editors. Polyesters III. Applications and commercial products). Biopolymers. 1st ed. Weinheim (Germany): Wiley-VCH Verlag GmbH; 2002. p. 1–23. and 129–177.
[4] Mecking S. Angew Chem Int Ed 2004;43(9):1078–85.
[5] Sodergard A, Stolt M. Prog Polym Sci 2002;27(6):1123–63.
[6] Auras R, Harte B, Selke S. Macromol Biosci 2004;4(9):835–64.
[7] Degée Ph, Dubois Ph. Recent advances in polylactide chemistry and materials science [on line edition]. In: Kirk-Othmer, editor. Encyclopedia of chemical technology. Hoboken (NJ): John Wiley & Sons; 2004.
[8] Narayanan N, Roychoudhury PK, Srivastava A. Electron J Biotechnol 2004;7(2):167–79.
[9] Ignjatovic N, Uskokovic D. Appl Surf Sci 2004;238(1–4):314–9.
[10] Hong Z, Zhang P, He C, Qiu X, Liu A, Chen L, et al. Biomaterials 2005;26(32):6296–304.
[11] Schiller C, Rasche C, Wehmoller M, Beckmann F, Eufinger H, Epple M, et al. Biomaterials 2004;25(7–8):1239–47.

[12] Niemelä T. Polym Degrad Stab 2005;89(3):492–500.
[13] Bleach NC, Nazhat SN, Tanner KE, Kellomäki M, Törmälä P. Biomaterials 2002;23(7):1579–85.
[14] Nicolazo C, Gautier H, Brandao MJ, Daculsi G, Merle C. Biomaterials 2003;24(2):255–62.
[15] Murariu M, Da Silva Ferreira A, Degée Ph, Alexandre M, Dubois Ph. Polymer 2007;48(9):2613–8.
[16] Pluta M, Murariu M, Da Silva Ferreira A, Alexandre M, Galeski A, Dubois Ph. J Polym Sci B Polym Phys 2007;45:2770–80.
[17] Gorrasi G, Vittoria V, Murariu M, Da Silva Ferreira A, Alexandre M. Dubois Ph. Biomacromolecules 2008;9(3):984–90.
[18] Miyata T, Masuko T. Polymer 1997;38(16):4003–9.
[19] Taubner V, Shishoo R. J Appl Polym Sci 2001;79(12):2128–35.
[20] Gupta B, Revagade N, Hilborn J. Prog Polym Sci 2007;32(4):455–82.
[21] Pluta M, Paul MA, Alexandre M, Dubois Ph. J Polym Sci B Polym Phys 2006;44(2):312–25.
[22] Celli A, Scandola M. Polymer 1992;33(13):2699–703.
[23] Cai H, Dave V, Gross RA, MacCarthy SP. J Polym Sci B Polym Phys 1996;34(16):2701–8.
[24] Tsuji H, Ikada Y. Polym Degrad Stab 2000;67(1):179–89.
[25] Kovler K. "Recycling of chemical gypsum in construction" – Power Point presentation, Faculty of Civil Engineering Technion – Israel Institute of Technology. Available from: <www.technion.ac.il>, 2008 (accessed 28.02.2008).
[26] Follner S, Wolter A, Preusser A, Indris S, Silber C, Follner H. Cryst Res Technol 2002;37(10):1075–87.
[27] Mandal KP, Mandal KT. Cem Concr Res 2002;32:313–6.
[28] Mori T. J Dent Res 1986;65(6):877–88.