

## NANOCOMPOSITES BASED ON GELATIN AND MONTMORILLONITE Morphological and thermal studies

J. F. Martucci, A. Vázquez and R. A. Ruseckaite\*

Research Institute of Material Science and Technology (INTEMA), J. B. Justo 4302, 7600 - Mar del Plata, Argentina

Model gelatin/montmorillonite (Ge/MMt) composites were obtained for a variety of unmodified clay concentrations and in the absence of additives, with the main goal of evaluating the effect of the morphologies developed on the composites thermal stability.

Morphologies turned from partially exfoliated to exfoliated/intercalated and eventually agglomerated with increasing clay loading, as was observed by atomic force microscopy. Formulations containing 3–10 mass% montmorillonite resulted in an enhancement of composites thermal stability due to stabilizing interactions between co-components, such as strong hydrogen-type bonds, in agreement with the partially exfoliated/intercalated morphologies. Higher clay concentrations showed lower stabilizing effect in agreement with the agglomerated structures developed and the less effective interactions between co-components.

**Keywords:** gelatin, montmorillonite, nanocomposite, thermal degradation

### Introduction

Polymer layered silicate nanocomposites (PLSN) have attracted industrial and research attention because of the enhancement in material properties, even at very low loading levels of filler due to the high aspect ratio of the filler and the nano – level interactions with the polymer matrix [1]. Montmorillonite (MMt), one of the most common smectite clays, is a promising reinforcing material, naturally abundant and toxin-free which can be used as one of the components for food, medical, cosmetic and healthcare recipients [2]. Therefore, the development of composites based on clay and natural or biodegradable polymer have strong promise in designing eco-friendly green nanocomposites for several applications with large improvements in terms of mechanical, thermal and barrier properties [3–7].

Commercially available proteins, such as gelatin, encounter nowadays application at the packaging sector due to their interesting properties, including film – forming ability, elasticity and effective gas barrier properties [8, 9]. However, by its self, gelatin is a poor choice and some properties including thermal resistance, swelling capacity and barrier properties have to be improved to fulfill the requirements for food packaging applications [10]. Several strategies have been proposed in the literature to overcome the above mentioned limitations and design gelatin-based materials with modulated properties according to the specific applications. The presence of reactive side groups in gelatin

makes possible the introduction of covalent bonds between polypeptide chain through chemical, enzymatic or physical crosslinking reactions [11–14, 16]. Other possibility is by compounding with environmentally friendly reinforcements such as natural fibers [15] and layered silicates [16, 17].

Cross-linked-gelatin/montmorillonite (Ge/MMt) nanocomposites plasticized with glycerol with enhanced thermal, mechanical and swelling properties were successfully prepared for the first time by Zheng *et al.* [16, 17]. However, the relationship between morphologies and thermal stability was poorly explored.

Our current work is focused on preparing gelatin/montmorillonite composite films intended to produce laminates with potential application at the packaging sector. The resulting biopackaging is anticipated to be environmentally compatible and degradable. Since these films will be submitted to heat cycles during processing operations, it is necessary to well understand the effect of the nanostructure on the thermal stability for their rational application and this is the main objective of this study.

In the present work gelatin/unmodified montmorillonite composites were synthesized in the absence of crosslinking agents and plasticizers in order to evaluate the effect of clay on thermal properties of the obtained films. The morphologies developed were analyzed by atomic force microscopy (AFM) and the thermal stability of the obtained materials was evaluated by thermogravimetric analysis (TG).

\* Author for correspondence: roxana@fi.mdp.edu.ar

## Experimental

### Materials

Bovine hide gelatin (Ge) type B was kindly supplied by Rousselot (Argentina), Bloom 150, pH 5.3. Unmodified montmorillonite ( $\text{Na}^+$  MMt) was purchased from Southern Clay Products Inc. (Texas, USA), under the trade name Cloisite  $\text{Na}^+$ . The cation-exchange capacity (CEC) was 92.6 meq/100 mg of clay and the interlayer distance was 1.17 nm (as it was determined by X-ray diffraction on the dried powder).

### Preparation of Ge/MMt composites

Ge/MMt composites were prepared by solution intercalation method [18]. This technique is based on a solvent system in which the polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Model Ge/MMt nanocomposites were synthesized by sonicating together an aqueous gelatin solution with an aqueous dispersion of commercial Cloisite  $\text{Na}^+$ , according with the procedure reported elsewhere [16]. Basically, 2 g of pure gelatin powder was dissolved in 20 mL of distilled water at 50°C under constant stirring (10 g/100 mL). In parallel, unmodified MMt suspensions were prepared by dispersing the desired amounts of clay (ranging from 0.01 to 0.4 g  $\text{Na}^+$  MMt) in 10 mL of distilled water at 50°C by sonication. Before mixing, the pH was adjusted to 7, above the isoelectric point (ip) of the gelatin. Aqueous suspension (10 mL) was then mixed with gelatin solutions (20 mL) at 50°C and under vigorous stirring, in order to produce mixtures with 1 to 15 mass% MMt. The resulting aqueous suspensions were then cast on teflonated plates (10 mm diameter) and dried at 35°C during 15 h.

### Methods

Thermal stability of Ge/MMt was analyzed by thermogravimetry (TG). Non-isothermal degradation measurements were performed in a Setaram 92-12 TG 92 thermal gravimetric analyzer. Tests were running from room temperature up to 800°C at 10°C  $\text{min}^{-1}$  and under helium in order to avoid thermo-oxidative reactions (15 mL  $\text{min}^{-1}$ ).

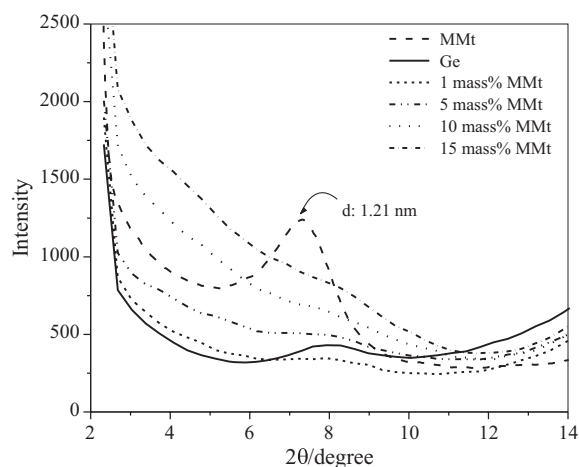
AFM (Nanoscope III a Multimode<sup>TM</sup> atomic force microscope, Digital Instruments) was used to examine composite morphologies. The microscope was allowed to equilibrate before testing at room temperature and kept at this temperature during all the experiments. Images were recorded in hard tapping mode (HTM-AFM) using an integrated silicon tip/cantilever (Digital Inst.) at

a frequency of 1 Hz. The Ge/MMt films were cross-sectioned under liquid nitrogen for obtaining smooth surfaces. All the images are shown without any further image processing treatment.

## Results and discussion

### Preparation and morphological analysis of Ge/MMt composites

Ge/MMt nanocomposites were obtained by mixing ultrasonically gelatin solutions and clay suspensions. The reaction parameters such as temperature, gelatin solution concentration, pH and sonication time were adjusted in order to produce exfoliated or intercalated nanocomposites. Temperature was fixed in 50°C in order to avoid triple helix renaturalization (which can act as physical crosslinking points). Concerning the pH, Zheng *et al.* [16] have reported that a pH above the gelatin isoelectric point favor the intercalation reaction. In the present work, a control experiment showed that pH 7 was enough for dispersing the silicate into the gelatin matrix. In the case of soluble polymers, the imposition of ultrasonic wave facilitated delamination process of layered silicates to achieve exfoliation. Composites with the above mentioned formulation were exposed to different sonication time and the resulting materials were evaluated by DRX. Figure 1 presents the DRX pattern of Ge/MMt composites with different clay contents, after 20 min of sonication. It can be seen that the original clay diffraction peak ( $2\theta=7.3^\circ$ ) almost vanishing in the composites. The broadening of the diffraction peak is associated with the presence of intercalated silicates along with exfoliated ones, or with disordered clay platelets dispersed in the composite [19]. It was experimentally found that lower sonication times (10 min) do not allow to exfoliate the clay for concen-



**Fig. 1** DRX pattern of Ge/MMt composites with different clay contents, after 20 min of sonication

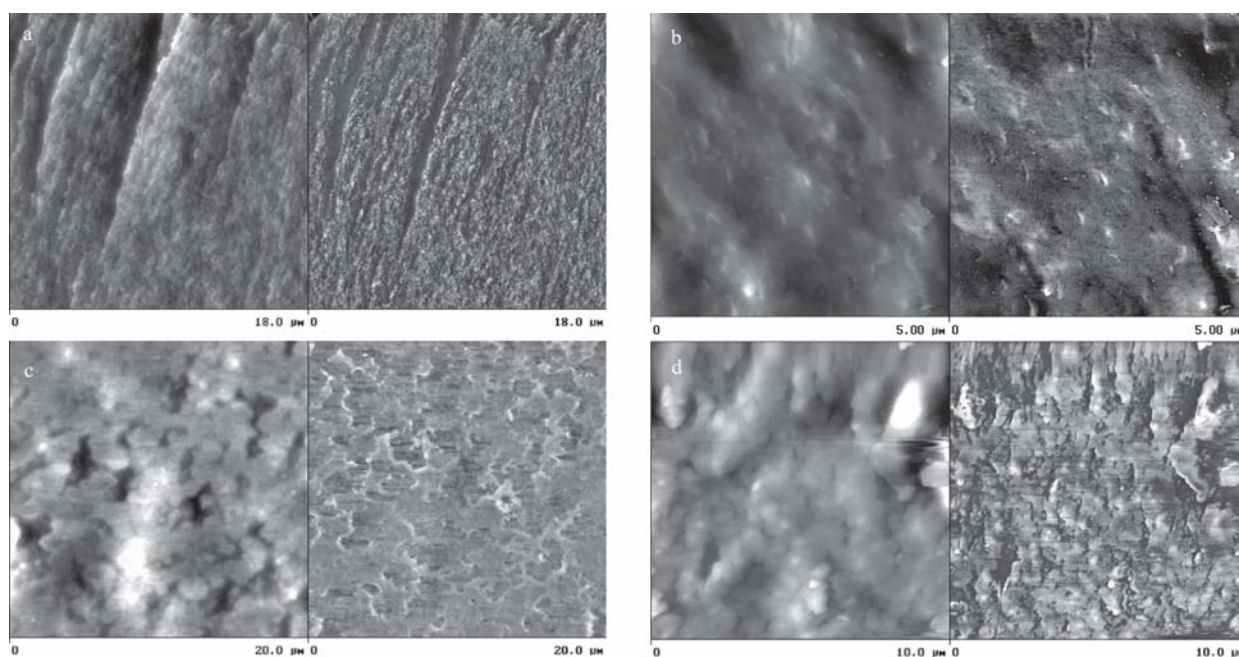
trations higher than 5 mass% MMt. Contrary, higher sonication times (30 min), conducted to agglomeration of clay nanoparticles. As a conclusion, the following conditions were fixed: gelatin concentration 10 g/100 mL, pH 7, MMt content less than 10 mass% and sonication time not longer than 20 min.

While DRX can provide information about the platelets separation, this technique fails once the nanoparticles exfoliate. Usually, transmission electronic microscopy (TEM) is used as complementary technique to visualize nanocomposite structures. However, TEM was not able to be applied on gelatin-based nanocomposites because ultramicrotoming procedure damages the sample. To further analyze the morphologies of gelatin-based nanocomposites, AFM was applied. This technique only requires a sample surface free of scratches or dust particles [20]. Figure 2 represents the HT-AFM height and phase images of pure gelatin and composites with different clay loading. The surface of pure gelatin film (Fig. 2a) shows some irregularities attributed to the casting process. In contrast, in the composites silicate particles are visible as light streaks in phase images (Figs 2b and c). AFM observations suggest that morphologies turn from exfoliated to exfoliated/intercalated or even agglomerated, as clay loading increases. Nanocomposite formation is mainly controlled by strong interactions such as coulombic forces between positives sites in the gelatin (i.e.  $\text{NH}_3^+$ ) and negative sites in galleries, and hydrogen interactions, between carbonyl groups in gelatin and hydroxyl groups within clay galleries [21]. Compos-

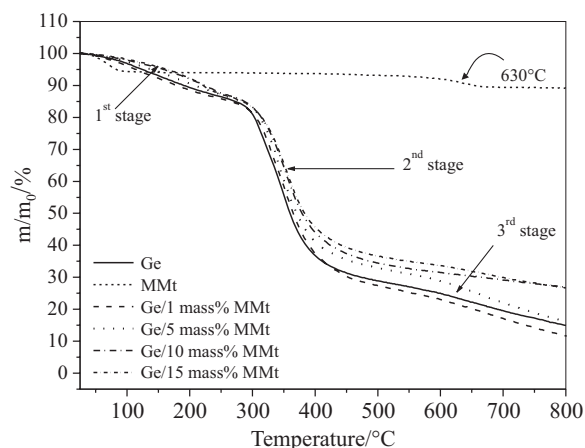
ites with 1 mass% MMt (Fig. 2b) show exfoliated structures, meanwhile Ge/5 mass% MMt (Fig. 2c) exhibit exfoliated/intercalated structures which are predominant up to clay contents of about 10 mass% MMt. Higher clay loading conducts to agglomerated platelets because exfoliation is hindered due to geometrical restrictions (Fig. 2d).

#### *Thermal degradation of pure components and Ge/MMt composites*

It is well reported for other polymer-unmodified montmorillonite systems that thermal stabilization depends on the extension of exfoliation/delamination as a function of clay content [3]. The effect of the nanofiller presence on the thermal stability of the composites was studied thermo-gravimetrically in inert atmosphere. The normalized dynamic curves for pure gelatin, montmorillonite and Ge/MMt composites (1–15 mass%) are depicted in Fig. 3. The TG curve of pure  $\text{Na}^+$ -MMt shows a main thermal event in the temperature range between 528–676°C and it is attributable to dehydroxylation of the clay layers [22]. As could be expected, the  $\text{Na}^+$  MMt shows a high thermal stability than pure gelatin film. Thermal decomposition of pure gelatin film is a gradual process with three main stages in the TG curve. The first one, in the range of 70–220°C, accounts for 11.1% mass loss and can be assigned to the loss of low molecular mass compounds, mainly adsorbed and bounded water. The second and main stage which extends up 410°C is related to the degradation of the protein



**Fig 2** In-phase HTM-AFM images (without any further treatment), of Ge/MMt films. a – pure Ge, b – Ge/1 mass% MMt, c – Ge/5 mass% MMt, d – Ge/15 mass% MMt



**Fig. 3** Normalized TG curves obtained in helium atmosphere and at  $10^{\circ}\text{C min}^{-1}$  for the pure components and composites

chain and accounts for 64% of mass loss [23, 24]. The higher temperature step ( $T > 600^{\circ}\text{C}$ ) can be attributed to the decomposition of more thermally stable structures due to crosslinking reactions produced during heating [23]. Cross-linking reactions may occur between hydroxyl groups and carboxylic acid formed by the chain scission, as in the case of polyamides [25].

The addition of nano-dispersed clay produces a delay in mass loss particularly within the temperature range of protein chain degradation ( $300\text{--}440^{\circ}\text{C}$ ) (Fig. 3). In order to analyze the effect of clay content on the thermal stability of gelatin films, experimental TG/DTG curves were used to obtain thermal parameters as a function of clay content. The temperature corresponding to initial of mass loss ( $T_0$ ) and the temperature of maximum rate of mass loss ( $T_{\text{max}}$ ), final residue at  $800^{\circ}\text{C}$  (mass%) and the integral procedural decomposition temperature values (IPDT) [26], which represents the overall nature of TG curves, are given in Table 1. The initial temperature of thermal decomposition is a very important parameter since it determines the maximum processing temperature which can be applied without thermally damage the material. Therefore,  $T_0$  can be considered as a criterion to evaluate the thermal stability of polymers. The higher the  $T_0$  value the higher the thermal stability of the polymer. Composites enhance their thermal stability with the addition of clay, as can be concluded from the shift of  $T_0$  and  $T_{\text{max}}$  toward higher values, being maximum for 10 mass% MMt (Table 1). It seems that exfoliated or partially exfoliated/intercalated nanostructures could be responsible for improving thermal stability of gelatin – based nanocomposites. When further increasing the filler content (i.e. 15 mass% MMt), only a slight increment in  $T_{\text{max}}$  is noticed, according to the agglomerated morphologies observed. These results are in accordance with those reported in the literature for other

polymer/unmodified  $\text{Na}^+$  MMt composites, such as EVA-based nanocomposites [27].

As it was above mentioned, IPDT values give us an idea of the relative stability of the composites taking into account the whole TG curve [26]. IPDT values increase up to 10 mass% MMt, in agreement with the shift in  $T_0$  and  $T_{\text{max}}$  for the main degradation step (Table 1). Beyond this level, marked decrease is observed which can be attributed to the heterogeneous distribution of the agglomerated particles within the gelatin matrix.

Last but not least, the percentage of char at  $800^{\circ}\text{C}$  (Table 1) shows that composites release less amount of volatiles as clay concentration increases up to 10 mass% MMt, in agreement with the decrease in gas diffusion due to the presence of the nanolayers dispersed within the matrix which acts as a heat barrier. Thus, it can be inferred that gelatin can be thermally stabilized by adding small amounts of montmorillonite (3–10 mass%), without any further additive.

It is generally thought that silicate layers have good barrier to gases such as oxygen and nitrogen [19]. Clays are believed to increase the barrier properties by creating a ‘tortuous path’ for the diffusion of the volatiles products through the matrix [3, 22]. On the other hand, strong-type interactions are critical for the formation of intercalated and exfoliated hybrids [28]. In the case of gelatin, its polyelectrolyte nature impose that nanocomposite formation is mainly controlled by strong hydrogen interactions between carbonyl groups in gelatin and hydroxyl groups in clay galleries, even at pHs higher than gelatin isoelectric point. Similar interactions were considered for other polyelectrolyte such as chitosan [29]. Thus, in order to give an explanation to the effect of clay on thermal stabilization of Ge/MMt composites, interactions between co-components were evaluated. An easy way to evaluate the presence of such interactions is by

**Table 1** Characteristic parameters of the thermal degradation of Ge/MMt composites

Sample name	Second stage (250–410°C)		Residue at 800°C/ mass%	IPDT <sup>c</sup> / °C
	$T_0$ /°C <sup>a</sup>	$T_{\text{max}}$ /°C <sup>b</sup>		
Ge	302	344	14.7	524
Ge/1 mass%	303	348	11.5	496
Ge/5 mass%	310	352	15.6	553
Ge/10 mass%	311	358	26.5	855
Ge/15 mass%	311	359	26.5	660

<sup>a</sup>Taken from the onset of the second stage decomposition process;

<sup>b</sup>maximum of the DTG curve for the second stage

<sup>c</sup>decomposition temperature

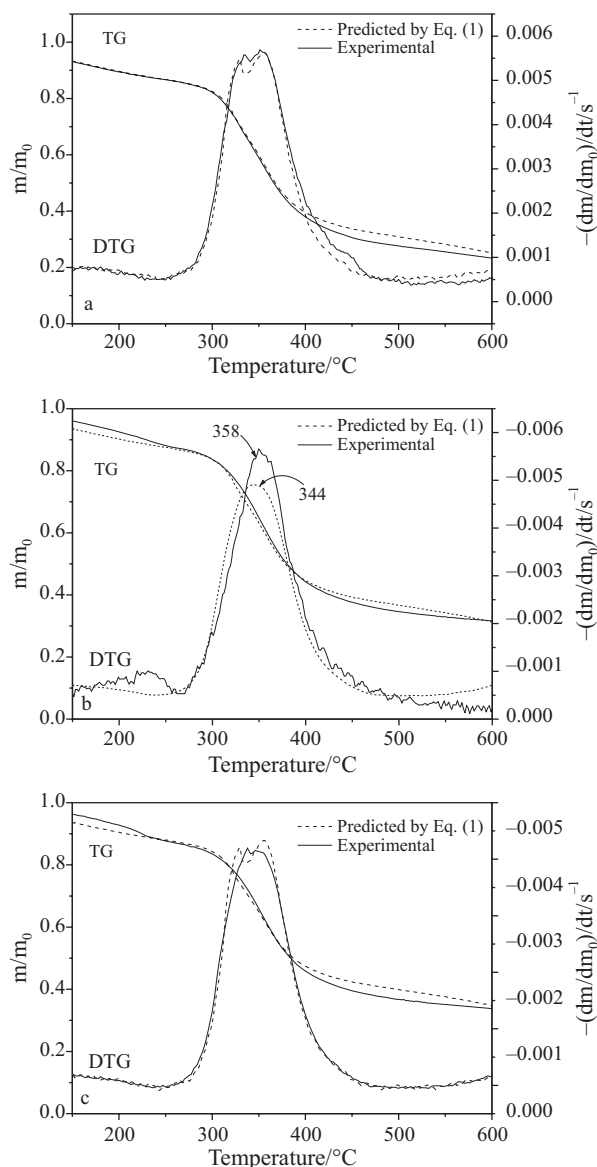
predicting TG/DTG curves as the sum of the individual components as follows [30]:

$$(m/m_0) = \sum_i Y_i (m/m_0)_i \quad (1)$$

where  $Y_i$  is the mass fraction of component  $i$ ,  $(m/m_0)_i$  is the normalized mass loss for component  $i$  derived from TG experiments for the individual components,  $j$  denotes the number of components in the actual mixture. Derivatives are obtained in the same way. If there is no interactions between co-components, experimental curves should be reproduced by Eq. (1). Calculated and experimental TG/DTG curves obtained in helium for Ge/composites are shown in Figs 4a–c. For low clay content (i.e. 1 mass% MMT, Fig. 4a), some slight discrepancies between experimental and calculated curves are observed specially at the end of the second stage of gelatin thermal degradation, but  $T_0$  and  $T_{\max}$  values do not change significantly. As clay loadings increases stabilizing/destabilizing interactions appear according with the temperature region. For 10 mass% MMT, positive deviations are predicted in almost the whole temperature range with higher values of  $T_0$  and  $T_{\max}$  (Table 1), which is an evidence that clay restrict the diffusion of gaseous products from the matrix degradation. Higher clay concentrations (Fig 4c), induce unfavorable interaction, mainly at higher temperatures. These results suggest that thermal stabilization can be obtained at clay content of 3 to 10 mass% MMT, being optimal for 10 mass%. Below this range no thermal stabilizing effect is observed meanwhile higher concentrations of filler conducts to a decrease in thermal stability. Once again the effect of the morphology is evident: Ge/1 mass% MMT conducts to exfoliated composites but the amount of clay sheets dispersed is not enough to produce any thermal improvement may be due to the low content of filler or inhomogeneous distribution within the nanocomposite; for clay content of 10 mass%, a slight stabilizing effect is observed according to the exfoliated/intercalated morphology obtained at least up to 10 mass% clay. Higher filler content conducts to agglomerated (microcomposite) structures which favor the interactions within each individual component over those between components, and no stabilizing effect is observed. Thus by controlling the clay content and synthesis conditions, Ge/MMT composites with enhanced thermal stability can be obtained.

## Conclusions

Model gelatin/montmorillonite nanocomposites with improved thermal stability were synthesized in the absence of plasticizers and crosslinking agent. Thermal behavior of Ge/MMT materials resulted to be inti-



**Fig. 4** Experimental and predicted DTG curves (Eq. (1)) for different clay content. a – 1 mass%, b – 10 mass%, c – 15 mass%

ately related with the clay content, and as a consequence, with the morphologies developed. AFM images of the cryo-fractured composites allowed us to establish the relationship between clay content and the extension of exfoliated, exfoliated/intercalated or agglomerated structures. The AFM images showed that exfoliated and exfoliated/intercalated morphologies can be obtained at filler loadings in the range of 1 to 10 mass%. Higher amounts of clay conducts to platelets agglomeration and materials evolved from nano to microcomposites. It is important to note that the best thermal parameters were obtained for formulations containing 3–10 mass% MMT, according with the observed partially exfoliated/intercalated structures. This result was not only attributed

to the inherent barrier properties of montmorillonite but to the stabilizing interactions between gelatin and clay, which can be related with the ‘physical crosslinking action’ of clay, mentioned by Yao *et al.* [16]. For clay loading in the range of 3 to 10 mass%, effective hydrogen-type interactions may take place due to the morphologies developed. Increasing amounts of filler favored platelets agglomeration and decreased Ge–MMt stabilizing interactions.

## Acknowledgements

The authors acknowledge the financial support of the National Research Council (CONICET, PIP 6258) and the Science and Technology Secretary (SECyT, PICT 12-15074) of Argentina. The authors wish to express their appreciation to Prof. Iñaki Mondragón Egaña of the Dpto de Ingeniería Química y Medio Ambiente, Escuela Universitaria Politécnica – Donostia, Universidad del País Vasco (España) for his useful advice.

## References

- S. S. Ray and M. Busmina, *Progress. Mater. Sci.*, 50 (2005) 962.
- H.-M. Park, X. Li, C.-Z. Jin, C.-Y. Park, W.-J. Cho and C.-S. Ha, *Macromol. Mater. Sci.*, 287 (2002) 553.
- M.-A. Paul, C. Delcourt, M. Alexandre, Ph. Degée, F. Monteverde and Ph. Dubois, *Polym. Degrad. Stab.*, 87 (2005) 535.
- B. Lepoittevin, N. Pantoustier, M. Devalckenaere, M. Alexandre, D. Kubies, C. Calberg, R. Jérôme and Ph. Dubois, *Macromolecules*, 35 (2002) 8385.
- G. Gorrasi, M. Tortora, V. Vittoria, E. Pollet, B. Lepoittevin M. Alexandre and Ph. Dubois, *Polymer*, 44 (2003) 2271.
- S. Wang, C. Song, G. Chen, T. Guo, J. Liu, B. Zhang and S. Takeuchi, *Polym. Degrad. Stab.*, 87 (2005) 696.
- M. Avella, J. J. de Vlieger, M. M. Errico, S. Fischer, P. Vacca and M. G. Volpe, *Food Chem.*, 93 (2005) 467.
- I. S. Arvanitoyannis, E. Psomiadou, A. Nakayama, S. Aiba and N. Yamamoto, *Food Chem.*, 60 (1997) 593.
- R.A. de Carvalho and C. R. F. Grosso, *Food Hydrocolloids*, 18 (2004) 717.
- K. S. Miller and J. M. Krochta, *Trends Food Sci. Technol.*, 8 (1997) 228.
- A. Bigi, M. Borghi, G. Cojazzi, A. M. Fichera, S. Panzavolta and N. Roveri, *J. Therm. Anal. Cal.*, 61 (2000) 451.
- A. J. Kuijpers, G. H. M. Engbers, J. Feijen, S. C. de Smedt, T. K. L. Meyvis, J. Demeester, J. Krijgsveld, S. A. J. Zaat and J. Dankert, *Macromolecules*, 32 (1999) 3325.
- J. Tanaka, S. Murabayashi and Y. Mitamura, *Mater. Sci. Eng. C*, 83 (2004) 781.
- B. Balakrishnan and A. Jayakrishnan, *Biomaterials*, 26 (2005) 3495.
- E. Chiellini, P. Cinelli, E. Grillo Fernández, El-Refaie Kenawy and A. Lazzeri, *Biomacromolecules*, 2 (2001) 806.
- J. P. Zheng, P. Li, Y. L. Ma and K. D. Yao, *J. Appl. Polym. Sci.*, 86 (2002) 1189.
- P. Li, J. P. Zheng, Y. L. Ma and K. D. Yao, *J. Appl. Polym. Sci.*, 88 (2003) 322.
- P. Le Baron, Z. Wang and T. J. Pinnavaia, *Appl. Clay Sci.*, 15 (1999) 11.
- T. X. Liu, Z. H. Liu, K. X. Ma, L. Shen, K. Y. Zeng and C. B. He, *Compos. Sci. Technol.*, 63 (2003) 331.
- B. Yalcin and M. Cakmak, *Polymer*, 45 (2004) 6623.
- A. De Cristofaro and A. Violante, *Appl. Clay Sci.*, 19 (2001) 59.
- K. P. Pramoda, T. Liu, Z. Liu, C. He and H.-J. Sue, *Polym. Degrad. Stab.*, 81 (2003) 47.
- P. M. L. Barreto, A. T. N. Pires and V. Soldi, *Polym. Degrad. Stab.*, 79 (2003) 147.
- A. Kaminska and A. Sionkowska, *Polym. Degrad. Stab.*, 65 (1999) 87.
- L. H. Peebles and M. H. Huffman, *J. Polym. Sci.*, A-1 (1971) 1807.
- C. D. Doyle, *Anal. Chem.*, 133 (1961) 77.
- S. T. Lim, Y. H. Hyun, H. J. Choi and M. S. Jhon, *Chem. Mater.*, 14 (2002) 1839.
- M. Darder, M. Colilla and E. Ruiz-Hitzky, *Chem. Mater.*, 15 (2003) 3774.
- S.-R. Lee, H.-M. Park, H. Lim, T. Kang, X. Li, W.-J. Cho and C.-S. Ha, *Polymer*, 43 (2002) 2495.
- Y. Matsuzawa, M. Ayabe and J. Nishino, *Polym. Degrad. Stab.*, 71 (2001) 435.

---

Received: November 28, 2005

Accepted: February 12, 2007

---

DOI: 10.1007/s10973-006-7454-0