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Physical Aging in Poly(L-lactide) and its Multi-Wall Carbon Nanotube Nanocomposites

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Summary: In this work the effects of the structure evolution of neat PLLA and its multi-wall carbon nanotube nanocomposites at an aging temperature of 45 °C (T_g-12 °C) have been investigated. The analysis of enthalpy relaxation rate (β_H) of composites by means of differential scanning calorimetry (DSC) reveals the existence of a critical concentration of 1.25–2.5 wt. % in which aging rate reaches a mi–imum value of 1.351 J/g. Mechanical tests showed that neat polymer is much more sensitive to the aging process than the reinforced one. As shown by transmission electron microscopy (TEM) all the samples present randomly dispersed nanotubes, yielding an agglomerated structure at MWCNT contents exceeding 1.25–2.5 wt.%. The obtained results are explained from the viewpoint of polymer/filler interfacial effects that perturb the structural relaxation of glassy polymer due to the drastic reduction on the molecular mobility of polymer chains in the vicinity of carbon nanotube surfaces. In this way, nanocomposite approach represents an efficient strategy to successfully reduce the physical aging process of polymers.

Keywords: carbon nanotubes; interfaces; microstructure; nanocomposites; relaxation

Introduction

The cooling of a polymer from the melt to temperatures below glass transition results in non-equilibrium state due to the fact that molecular mobility slows down below *Tg*. This metastable glassy material has higher specific volume, enthalpy and entropy than the polymer in its corresponding equilibrium state. The thermodynamic equilibrium is reached by means of chain-conformation changes, which is often referred as physical aging.[1] During this rearrangement of polymer chains the macroscopic properties can change drastically, limiting the stability of polymeric materials.[2] Therefore, the reduction of physical aging rate is essential for prospective applications since longer lifetime and more reliable materials can be obtained. In this way, some authors have found that the inclusion of nanoreinforcements into polymeric materials reduce the physical aging rate of polymers.[3–5] It had been reported that the numerous filler/matrix interfaces existing in composites can be used to control the structural evolution of polymers during aging.[6] Polylactides are important medical plastics[7] due to the fact that they are biocompatible and bioresorbable. In addition, recent progress in production of Poly (L-lactide) (PLLA) at low cost is accelerating its use as a commodity plastic for ecological packaging applications. In this work we demonstrate that the physical aging process of PLLA can be successfully delayed by means of the inclusion carbon nanotubes (CNT). Due to the large surface area of carbon nanotubes the incorporated surfaces interfere favourably with the process of polymer conformational changes leading to physical aging, thus PLLA-based materials with improved properties can be obtained. For instance, the synergetic effect obtained from combination of thermally insulating polymers and carbon nanotubes

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opens new insights for the development of thermally and electrically conductive composite materials,[8,9] for example to be used as thermal interface materials, heat sinks, solar cells, etc. Thus, in this work physical aging of PLLA and its multi-wall carbon nanotube composites at 45 °C (T_g-12 °C) is studied as a kinetic process on the basis of molecular chain relaxation effects.

Experimental Part

PLLA (Biomer®, Germany) with a number-average molecular weight (M_n) of 153.000 g/mol was used as the matrix. The carbon nanotubes used were MWCNT (Graphistrenght™ C100) with a length between 0.1 and 10 μm, outer mean diameter in the range of 10–15 nm and a specific area of 229 m^2/g. The polymer-matrix nanocomposites were prepared by mixing PLLA pellets and the desired amount of MWCNT using a Brabender Plasti-Coder PL2000 melt-mixer at 200 °C for 5 min (50 rpm). Obtained mixtures were fabricated into 1 mm thick films by hot pressing at 200 °C for 4 min at a pressure of 240 MPa. Melted films were quenched in cold water. In this way, any further development of the crystalline structure of PLLA is prevented.

Discussion

Enthalpy relaxation experiments of composites were carried out on a DSC in order to determine the effects of the addition of carbon nanotubes on the segmental motion of PLLA. As shown in the inset of Figure 1, aged specimens showed a characteristic endothermic overshoot at the glass transition. For instance, the measured enthalpy relaxation for neat PLLA after aging for 10 minutes is 0.496 Jg^{-1}, whereas the enthalpy corresponding to the sample aged for 800 minutes is 3.923 Jg^{-1}. Longer aging times (t_a) resulted in a systematical increase of the enthalpy relaxation, yielding also a shift to higher temperatures of the endothermic peak. As the polymer evolves towards equilibrium more energy is needed for the glass transition, resulting in a larger endothermic peak and a shift of the glass transition to higher temperatures.[10] In order to directly quantify the overall segmental relaxation rate of polylactide chains within composites, the enthalpy relaxation rate β_H was calculated as follows:

$$\beta_H = \left[\frac{\partial \delta_H}{\partial(\log t_a)}\right]_{q_1,q_2,T_a} \tag{1}$$

where q_1 is the cooling rate (30 °C/min), q_2 is the heating rate (10 °C/min), T_a is the annealing temperature (45 °C), t_a is the

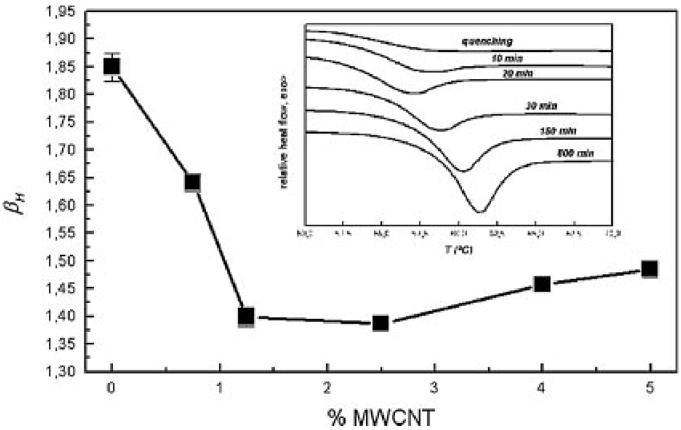

Figure 1.

Dependence of enthalpy loss rate (β_H) on the nanotube concentration. Inset shows the DSC heating scan at Tg region for PLLA/MWCNT 4 wt % nanocomposite aged at 45 °C for different times.

aging time and δ_H is the enthalpy loss. By fixing these variables, the enthalpy relaxation of nanocomposites may be only related to the addition of carbon nanotubes. β_H normalized values are shown in Figure 1 depending on the nanotube concentration. Experimental results reveal slower aging dynamics in the presence of CNT (as indicated by the lowering of β_H), suggesting that the addition of carbon nanotubes within PLLA results in restricted chain mobility in the vicinity of polymer/nanotube interfaces. For instance, the addition of 2.5 wt % results in a reduction of 27% of the enthalpy relaxation rate. Moreover, larger concentrations than 2.5 wt % result in a reduction of the efficiency of carbon nanotubes as effective constraining elements for polymer rearrangement, increasing again the enthalpy relaxation rate from 1.386 J/g for 2.5 wt % MWCNT up to 1.485 J/g for the 5 wt % composite. This may be due to the aggregation effects which yield a reduction of the available interfaces exposed to polymer chains, resulting in a reduction of the efficiency of CNT as effective constraining elements for the rearrangement of polymer chains.

Dynamic mechanical analysis (DMA) and tensile tests were carried out in order to analyze the effect of the PLLA phase-structure evolution on the mechanical properties of composites. The temperature dependence of loss tangent for neat PLLA and its 1.25 wt % composite aged at 45 °C in function of time is shown in Figure 2. It can be clearly seen that for both PLLA and its 1.25 wt % composites, the maximum of *tan δ* shifts to higher temperatures as aging time increases. This behaviour is accompanied with an increase in the maximum *tan δ* and with a decrease of the peak width during aging. It is worth to note that the displacement and the height of *tan δ* of neat polymer is more pronounced of the reinforced samples. For instance, the glass transition temperature of the unreinforced polymer steeply increases form 61.24 °C to 65.07 °C, while for its 1.25 wt % composite only increased from 61.97 °C to 64.33 °C. Those results may be correlated with different sensitivities to the physical aging process of the neat and reinforced samples, indicating that carbon nanotubes interfere chain relaxation, yielding a reduction in the overall aging rate of composites with regard to unreinforced PLLA. Those results agree well with DSC analysis, from which slower physical aging dynamics in the presence of carbon nanotubes was also observed.

Figure 3 shows the stress-strain curves of aged PLLA and its 1.25 wt % nanocomposite. It is worth to note that for a given aging time, specimens containing carbon nanotubes are seen to be stiffer, indicating that carbon nanotubes are acting as efficient reinforcement elements. Moreover, for both compositions, i.e. neat PLLA and its 1.25 wt. % composite, the increase in Young's modulus during the aging is accompanied by a decrease in both strain at yield (ε_y) and strain at break (ε_r). For instance, the Young's modulus, yield strain and break strain of unaged PLLA are 974 MPa, 9.66% and 47.91% as compared to those of PLLA aged for 6100 minutes which are 1085 MPa, 8.43% and 9.37% respectively. Aging of a polymer results in increased chain stiffness, increased density and loss of free volume, leading to embrittlement of samples.[11] It is worth to note that the changes induced on the mechanical properties during the aging process (Young's modulus of samples is increased through thermal aging up to 11.4% for neat PLLA and 6.1% for PLLA/MWCNT 1.25 wt % composite in regard to the as-quenched specimens) are much more significant for the unreinforced sample. The interfaces provided by MWCNT act as effective constraining elements in which polymer chains are attached to the nanotube surface, resulting in a retardation of the polylactide chain relaxation mechanisms towards equilibrium. In this way, smaller changes in mechanical properties of composites for a given aging time in regard to those for the unreinforced polymer are achieved.

TEM micrographs (Figure 4) show a good distribution of MWCNT within PLLA matrix, i.e., at low concentrations, each

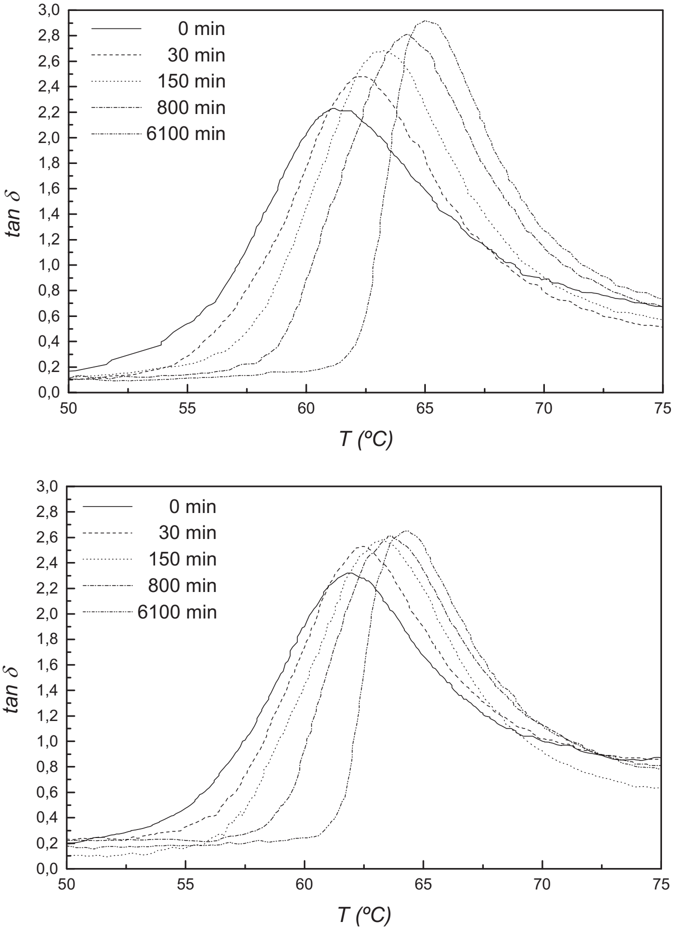

Figure 2.
Temperature dependence of *tan δ* of aged PLLA and its 1.25 wt % composite.

nanotube provides interfaces along their length. However, for larger concentrations than a critical value aggregation gives rise to entanglements among adjacent CNT, resulting in a reduction of the surface area of nanotubes that remains exposed to polymer chains, hence reducing their efficiency as constraining elements. Thus, there is a critical concentration in which a maximum nanotube/polymer interface is achieved. The transition from well dispersed distribution of MWCNT to aggregate structure is produced for a composition comprised between 1.25 and 2.5 wt % MWCNT.

A model for the structural relaxation mechanism of polymer chains within PLLA/MWCNT nanocomposites is proposed on the basis of the obtained results. In Figure 5 PLLA chains are represented as thin dotted black lines, MWCNT are represented as blue rods and nanotube/polymer interfaces are represented as brown surrounding areas. The aging process in neat PLLA takes place without restrictions as polymer chains are randomly distributed in the amorphous state. The existence of the interfaces provided by the addition of 0.75 wt % MWCNT, however, provides constraining surfaces that interfere the relaxation of polymer chains, leading to a reduction of the bulk aging rate.

It is worth to note that the reported change on the structural relaxation of

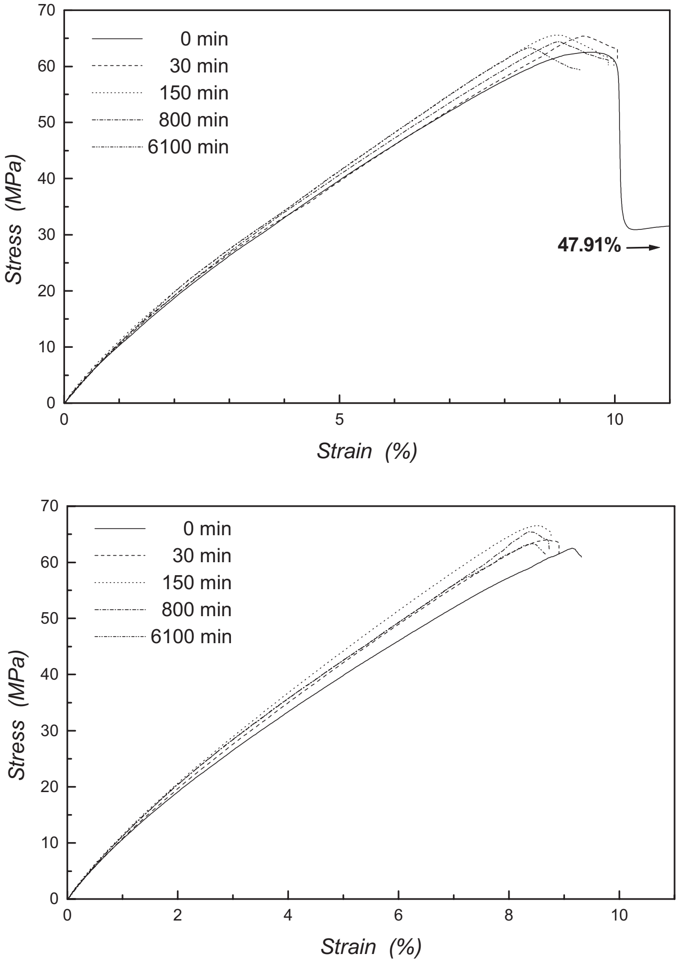

Figure 3.
Tensile curves pure PLLA and its 1.25 wt. % composite aged at 45 °C for different times.

polymer chains may be related to the relative distance from the nanotube surface. In this way, since the relaxation of polymer chains is suppressed in the vicinity of nanotube surface,[6] an increase of the amount of polymer/CNT interfaces would yield a reduction of the overall physical aging rate of composite. As a consequence,

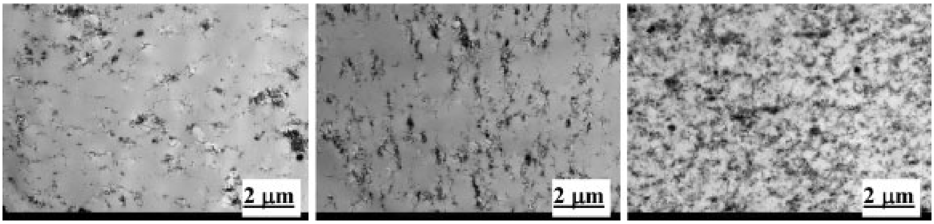

Figure 4.
TEM micrographs showing carbon nanotube dispersion of PLLA/MWCNT composites having the following MWCNT wt.%: a) 0.75; b) 1.25 and c) 4.

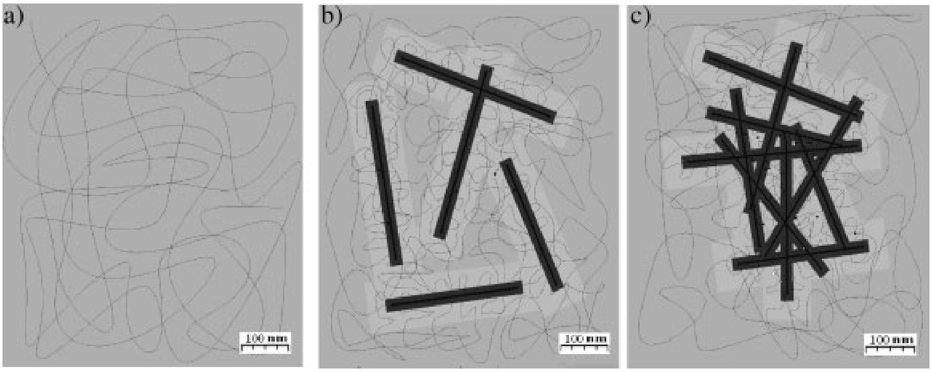

Figure 5.
Schematical representation of physical aging mechanism within PLLA and its PLLA/MWCNT composites: a) neat PLLA; b) 0.75 wt % MWCNT; c) 1.25 wt % MWCNT and d) 4 wt % MWCNT.

larger concentrations than 1.25-2.5 wt % result in an increase of direct contacts between individual nanotubes and trend to form bundles that reduce matrix-nanotube contact area per single MWCNT,[12] reducing the efficiency of carbon nanotubes to perturb the structural relaxation of PLLA. Results obtained in this work through DSC, DMA and tensile test analysis demonstrate that the amount of polymer/MWCNT interfaces in our composites are large enough to decrease the bulk physical aging rate of PLLA, unlike what was observed in a previous work.[13]

Conclusion

Physical aging rate was reduced with the addition of CNT, suggesting that carbon nanotubes delay the ability of chains to attain a state closer to thermodynamic equilibrium. This may be due to the many polymer-filler interfaces that perturb the structural relaxation at a glassy-state ($T = 45\,^{\circ}\mathrm{C}$), hence reducing aging of PLLA. The results obtained with PLLA/MWCNT composites suggest that the development of nanocomposite systems can be viewed as a good strategy to delay the aging process of polymers.

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[1] J. Kurchan, *Nature* **2005**, *433*, 222.
[2] Z. Hongxia, E. A. Lofgren, S. A. Jabarin, *J. Appl. Polym. Sci.* **2009**, *112*, 2906.
[3] A. Lee, J. D. Lichtenhan, *Macromolecules* **1998**, *31*, 4970.
[4] H. Lu, S. Nutt, *Macromol. Chem. Phys.* **2003**, *204*, 1832.
[5] H. Lu, S. Nutt, *Macromolecules* **2003**, *36*, 4010.
[6] R. D. Priestley, C. J. Ellison, L. J. Broadbelt, J. M. Torkelson, *Science* **2005**, *309*, 456.
[7] M. Martina, D. W. Hutmacher, *Polymer International* **2007**, *56*, 145.
[8] E. Lizundia, A. Oleaga, A. Salazar, J. R. Sarasua, *Polymer* **2012**, DOI: 10.1016/j.polymer.2012.03.046.
[9] E. Lizundia, J. R. Sarasua, F. D'Angelo, A. Orlacchio, S. Martino, J. M. Kenny, I. Armentano, *Macromolecular Bioscience* **2012**, DOI: 10.1002/mabi.201200008.
[10] J. M. Hutchinson, S. Smith, B. Horne, G. M. Gourlay, *Macromolecules* **1999**, *32*, 5046.
[11] P. Pan, B. Zhu, Y. Inoue, *Macromolecules* **2007**, *40*, 9664.
[12] A. A. Koval'chuk, A. N. Shchegolikhin, V. G. Shevchenk, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *Macromolecules* **2008**, *41*, 3149.
[13] A. Y. H. Liu, J. Rottler, *Journal of Polymer Science: Part B: Polymer Physics* **2009**, *47*, 1789.