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Carbon nanotubes in blends of polycaprolactone/thermoplastic starch

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ABSTRACT

Despite the importance of polymer–polymer multiphase systems, very little work has been carried out on the preferred localization of solid inclusions in such multiphase systems. In this work, carbon nanotubes (CNT) are dispersed with polycaprolactone (PCL) and thermoplastic starch (TPS) at several CNT contents via a combined solution/twin-screw extrusion melt mixing method. A PCL/CNT masterbatch was first prepared and then blended with 20 wt% TPS. Transmission and scanning electron microscopy images reveal a CNT localization principally in the TPS phase and partly at the PCL/TPS interface, with no further change by annealing. This indicates a strong driving force for the CNTs toward TPS. Young's model predicts that the nanotubes should be located at the interface. X-ray photoelectron spectroscopy (XPS) of extracted CNTs quantitatively confirms an encapsulation by TPS and reveals a covalent bonding of CNTs with thermoplastic starch. It appears likely that the nanotubes migrate to the interface, react with TPS and then are subsequently drawn into the low viscosity TPS phase. In a low shear rate/low shear stress internal mixer the nanotubes are found both in the PCL phase and at the PCL/TPS interface and have not completed the transit to the TPS phase. This latter result indicates the importance of choosing appropriate processing conditions in order to minimize kinetic effects. The addition of CNTs to PCL results in an increase in the crystallization temperature and a decrease in the percent crystallinity confirming the heterogeneous nucleating effect of the nanotubes. Finally, DMA analysis reveals a dramatic decrease in the starch rich phase transition temperature (~26 °C), for the system with nanotubes located in the TPS phase.

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1. Introduction

Bioplastics include polymers that are biodegradable, e.g. polycaprolactone (PCL), or biobased, such as biobased polyethylene, or both such as thermoplastic starch (TPS) and PHAs (Queiroz & Collares-Queiroz, 2009). Despite their high annual growth rates, most bioplastics suffer from their inability to cover a broad range of mechanical properties in comparison with the commodity plastics; e.g. PLA or PHB show high modulus, but very low elongation at breaks; PCL demonstrates excellent ductility but suffers from low modulus. Among them, thermoplastic starch (TPS), a widely available biobased material with reasonable cost and excellent biodegradation properties, has been significantly studied (Averous, 2004). Thermoplastic starch can easily flow at high temperatures and be melt processed in a similar fashion to other thermoplastic polymers. The major drawback of TPS, however, is its susceptibility to humidity and weak mechanical properties which generally limits its use in pure form and requires it to be blended with other polymers.

PCL has been used in soft compostable packaging (Averous, 2004) as well as in tissue engineering applications (Bajgai et al., 2008). It has hydrophobic characteristics and shows excellent ductility. However, it is a petroleum based polymer with a low degradation rate and several copolymers such as DL-lactide or glycolide have been incorporated in the structure of PCL to improve its degradation properties (Nair & Laurencin, 2007). Additionally, the degradation rate of polycaprolactone has been shown to be significantly improved in presence of starch (Shin, Lee, Shin, Balakrishnan, & Narayan, 2004). The blending of PCL with thermoplastic starch will increase the biobased portion/biodegradation rate of the PCL products. Several groups have already studied blends of PCL/TPS and have reported a complete immiscibility between the two polymers. Averous, Moro, Dole and Fringant (2000) have shown complete incompatibility of the two pairs based on T_g curves, however, significant improvements in the mechanical properties of TPS were observed. In a recent work in this laboratory (Li & Favis, 2010), the incorporation of TPS in a PCL matrix was shown to result in very fine and stable morphologies. These TPS/PCL blends demonstrated a high ductility at values as high as 50 wt% TPS and a corresponding drop in the modulus compared to neat PCL. This level of morphology control can be used as a starting point to evaluate the effect of the incorporation of solid nanoinclusions

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as a route toward higher performance materials. Owing to the superior mechanical, electrical, magnetic, optical and thermal properties of carbon nanotubes (CNT), they offer the potential to generate novel materials when properly dispersed in a polymer resin (Moniruzzaman & Winey, 2006). In recent years carbon nanotubes have been successfully added to polymer blends improving the morphology and/or mechanical properties. However, any possible improvement introduced to the polymer blends is highly dependent on the level of dispersion and their localization. There are two factors influencing the nanoparticles localization: thermodynamics and kinetic effects. Ideally, CNTs will migrate to the phase with which they have the lowest interfacial tension in order to minimize the free energy of the system (thermodynamic effect) (Fenouillot, Cassagnau, & Majeste, 2009). This will lead to a stable dispersion which is expected to remain unchanged even by further processing. Goeldel, Kasaliwal and Poetschke (2009) showed that nanotubes can migrate to their thermodynamically favorable phase (i.e. PC in PC/SAN blends), irrespective of the mixing strategy. Several authors have tried to predict the localization of nanoparticles in polymer blends by calculating the interfacial tensions between the blend components (Elias, Fenouillot, Majeste, & Cassagnau, 2007; Katada, Buys, Tominaga, Asai, & Sumita, 2005). However, the evaluation of the interfacial tensions of polymers/solid inclusions is complex and has not been examined significantly in the literature. A rough estimation of the interfacial tensions can limit the ability to predict the localization in all cases (Wu et al., 2011).

Another determining factor related to the localization of nanofillers in polymeric systems is kinetics. Kinetics include processing parameters such as mixing sequence and shear rate as well as the viscosity, temperature, or even the shape of the nanofiller (Fenouillot et al., 2009; Goeldel, Kasaliwal, Poetschke, & Heinrich, 2012). Each of these may suppress the migration of the nanofillers to the thermodynamically stable state of dispersion, for example, an increased viscosity of PCL in PCL/PLA blends (Wu et al., 2011) or PMMA in PMMA/PP blends (Feng, Chan, & Li, 2003).

There are several methods for the dispersion of nanotubes in polymer matrix. Generally, the solvent dissolution method is shown to be one of the most efficient methods to disperse nanotubes in polymers but is mostly applicable at the laboratory scale (Grady, 2010). Melt mixing is the preferred method in spite of its lower comparative efficacy (Bose, Bhattacharyya, Bondre, Kulkarni, & Potschke, 2008; Goeldel et al., 2012). A combination of these methods may result in a high level of dispersion without damaging the nanotubes as is observed in masterbatch-type processes (Abbasi, Carreau, & Derdouri, 2010). It is expected that kinetic effects will be different depending on the type of mixing equipment with their different flow fields and intensity or processing times and hence, the localization of the nanoparticles may be potentially different in different mixing equipments (Breuer & Sundararaj, 2004).

The objective of this work is to investigate the localization of carbon nanotubes in blends of thermoplastic starch/polycaprolactone. Two melt blending operations will be examined. The observed localization of carbon nanotubes in the multiphase system will be compared to predictive models and the relative role of thermodynamic and kinetic effects will be addressed. The influence of carbon nanotubes on the morphology of the blend will be studied. Finally, the influence of carbon nanotubes on the physical properties of the material will be assessed.

2. Experimental

2.1. Materials

The native wheat starch and glycerol were obtained from ADM and Labmat, respectively. The wheat starch was composed of 25% amylose and 75% amylopectin. The glycerol was pure at 99.5% and contained 0.5% water. Polycaprolactone (PCL), CAPA 6500, was supplied by Solvay Chemicals. Capa6500 has a molecular weight of 50,000 g mol^{-1} and a MFI of 7.0 (g per 10 min, 160 °C). Surface modified multiwall carbon nanotubes (NC3101) were purchased from Nanocyl Co. The average diameter and length of CNTs were 9.5 nm and 1.5 μm, respectively with a carbon purity of greater than 95%. The carboxylic acid surface modification was evaluated by XPS to be ~4%.

2.2. PCL/CNT preparation

A PCL–CNT masterbatch was first prepared at high CNT loadings (9–11 wt%) through a solution casting method at room temperature. Nanotubes were dispersed in THF for 1 h via ultrasonication. Then the PCL/THF solution was added to CNT solution and ultrasonication continued for 1 h more. An antisolvent was added to the solution at the end and precipitated PCL and CNT were dried in the vacuum oven at 35 °C for a week. The nanotubes wt% in the masterbatches was determined by TGA (TGA Q500, TA Universal).

2.3. Blend preparation

2.3.1. Twin-screw

The PCL/CNT masterbatch then went through two different methods of preparation. In method one, TPS/PCL blends were prepared in a twin screw extruder via an established method in this laboratory (Favis, Rodriguez-Gonzalez, & Ramsay, 2003; Favis, Rodriguez-Gonzalez, & Ramsay, 2005) which consists of a single screw extruder (SSE) connected midway to a co-rotating twin screw extruder (TSE). The starch/glycerol/water suspension was fed to the TSE in which native starch was gelatinized and plasticized and the water was extracted before molten PCL/CNT are fed from the SSE to midway on the TSE. The TPS slurry was formulated in a way that the final TPS consists of 36 wt% glycerol. The compositions were all constant at PCL/TPS: 80/20 wt%. The screw speed was set at 100 rpm and the mixing zone temperatures were fixed at 145 °C. In order to obtain the CNT content of the blends, in each step thermogravimetric analyses (TGA) tests were conducted. CNT contents were 0.5 and 1 wt% based on the whole blend.

2.3.2. Brabender

In a second blending method, pure TPS was obtained via the above method in a twin screw extruder (Favis et al., 2003, 2005). The blend with PCL was then prepared via an internal mixer (Brabender Plasticorder). The rotor speed was set at 100 rpm and the processing temperature was at 145 °C. The master batch and neat PCL were then first fed to an internal mixer and after reaching plateau of the torque, thermoplastic starch (TPS) was added to the chamber. The compositions were all constant in PCL/TPS: 80/20 wt%. CNT contents were 0.5, 1 and 2 wt% based on the whole blend.

In order to prepare the samples for further characterization tests, the samples of both methods were compression molded at 145 °C. In order to be able to easily remove the samples, two Teflon sheets were inserted between metal plaques and molds. The total molding process time took 8 min under a nitrogen atmosphere after which it was quenched in a cold press to freeze-in the morphology.

Quiescent annealing was further conducted on some selected samples of both processing methods at 145 °C for up to 60 min.

2.4. Rheological characteristics

Rheological characterizations of the thermoplastic starch and PCL were performed in oscillation mode using a MCR-301 strain controlled rheometer from *Anton Paar*. The experiments were

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