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Elastic properties prediction of nano-clay reinforced polymer using multi-scale modeling based on a multi-scale characterization

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A B S T R A C T

This study aims at linking micro-structure key parameters with the measured macroscopic properties of nano-clay reinforced Poly(lactic acid) (PLA) and Poly(carbonate) (PC) through multi-scale sensitive mechanical model. Nano-clay platelets domain size and distribution were investigated using TEM observation. In case of intercalation, d-spacing between nano-platelets were measured using X-ray diffraction. Platelets domain size along with distance between platelets within the platelets stack were used as inputs for micro-mechanical models. To predict the macroscopic elastic properties, three approaches were considered; hybrid, matrix-inclusion models and their combinations. This last approach allows to take into account intercalated micro-structure by replacing the platelets properties by a stack of bi-layered sandwiches made of nano-clay platelets and polymer layers. Experimentally measured Young's modulus were well bounded by the model predictions.

1. Introduction

Because of their weight gain, reinforced polymers are increasingly used as structural materials. However, their weak mechanical and thermal properties are their most important limitations. To overcome these limitations, nano-metric particles can be used as reinforcing phase (Usuki et al., 1993; Kojima et al., 1993). Due to their nano-metric size, they present a high surface contact with the polymeric matrix. The large contact surface along with high mechanical properties lead to stiffer materials and lighter structures (low weight fraction of reinforcement, <10%) compared to classic reinforced polymers (Liu et al., 2009; Cauvin et al., 2010). As we have a heterogeneous material, micro-mechanical models could be used to predict their macroscopic properties. These approaches gave satisfying results for materials that are similarly heterogeneous (Mori and Tanaka, 1973) but at a larger length scale than nano-composites. As multi-scale models are a desired tool to predict properties of nano-reinforced materials, the use of these models requires a detailed knowledge of the micro/nano-structure. Different multi-scale approaches exist based either on Eshelby theory (matrix–inclusion) (Eshelby, 1957; Mori and Tanaka, 1973; Ponte Castañeda and Willis, 1995) or hybrid models (van Dommelen et al., 2003) and also 3-D finite element approach (Pahlavanpour et al., 2014). Each approach has its limitations due to the stated hypothesis (Zaïri et al., 2011; Cauvin et al., 2010; Fornes and Paul, 2003; Bédoui and Cauvin, 2012; Diani et al., 2008; Pahlavanpour et al., 2014). In this paper we will combine hybrid and

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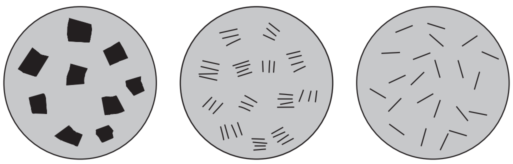
matrix–inclusion models, to take into account possible micro-structures: exfoliation, intercalation or aggregation (see Fig. 1(a)–(c)). These models should allow to predict the mechanical properties of nano-composites related to their micro-structures. We propose to consider multi-scale characterization to investigate the materials microstructure at different length-scales. This approach is meant to bring the appropriate input parameters for the developed micro-mechanical models to help predict or bound the experimental data with realistic mirostructural paramaters.

2. Materials and methods

2.1. Materials preparation

Two commercially available polymers were used. The first is the Poly(lactic acid), a PLA (Pli003) for extrusion and injection molding, provided by Natureplast, France. The second is the Poly(carbonate), a PC (PC920A) for extrusion and injection molding, provided by Sabic, USA. The organo-clay platelets used in this study are Cloisite 30B and Cloisite 93A produced by Southern Clay Products, USA. The Cloisite 30B and Cloisite 93A are montmorillonite modified with a quaternary ammonium salt. All the materials and references used in this study are summarized in Table 1 as well as the volume fraction corresponding to the weight fraction for each prepared nano-reinforced polymer. The weight fraction were determined by using Thermogravimetry Analysis (TGA) and densimetry measurements when possible (Table 1) to determine the nano-platelets volume fraction.

Polymers with nano-clay platelets were mixed using a twin-screw extruder, Eurolab 16. Configuration of the screw was fixed (mixing and conveying zone). Speed of screw (300 rpm) and temperatures (290 °C for PC and 200 °C for PLA) were fixed for all materials in order to have the same shearing conditions and a sufficient fluidity of the mixture (polymer + nano-clay). Clay were introduced in the second feeding port in the melted polymer. Obtained pellets were dried then injected-molded using Haake mini-Jet injection machine. Temperatures used for injection were the same temperatures used for extrusion. Moreover the temperatures of the mold was controlled at 100 °C for PC and 70 °C for PLA to help easily unmold the samples. As the process conditions are fixed for all the composites of this study, the dispersion of nano-clay in the polymeric matrix will depend on the compatibility between the nano-clay and the polymer (Maiti et al., 2002; Nieddu et al., 2009; Carrasco et al., 2011; Najafi et al., 2012).



(a) Aggregated (b) Intercalated (c) Exfoliated

Fig. 1. Different morphologies of nano-composites.

2.2. Mechanical properties

The Young's modulus was determined in accordance with ISO 527 Standard. Strain and stress were measured by an extensometer (Instron 10 mm-10%) and using a 5 kN load cell (Instron 5 kN) mounted on a tensile Zwick 4505 machine.

2.3. TEM

Microtomed slices (60 nm thickness) were prepared using PC-Power Tome micro-tome and mounted on carbon mesh (CF400-Cu-with carbon film). Samples were cut along and perpendicular to the injection direction. Observations were made using TEM (Tesla Bs500) with 90 kV voltage. In order to measure more accurately the nano-clay domain size, the Sobel filter implemented in ImageJ software (Rasband, 2011) was used and helped to increase the contrast between the matrix and the clay platelets.

2.4. X-ray diffraction

X-ray measurements were conducted under synchrotron sources at Advanced Photon Source at Argonne national laboratory (USA) on 5-ID-D beam-line. Medium angle detector was used with range of $0.12 \leqslant q \leqslant 0.70$ Å^{-1}.

2.5. Modeling

2.5.1. Matrix–inclusion models

Matrix–inclusion configuration was often used to represent the nano-composites morphology (Fornes and Paul, 2003; Zaïri et al., 2011; Bédoui and Cauvin, 2012). The Mori–Tanaka scheme (Mori and Tanaka, 1973) is a

Table 1
Weight fraction, volume fraction and samples references of the processed and tested materials in this study.

PC + 93A	fr (%wt)	0	–	1.24	2.66	–	3.68	–	–
	fr (%vol.)	0	–	0.79	1.70	–	2.36	–	–
	References	C0	–	C2	C3	–	C5	–	–
PLA + 30B	fr (%wt)	0	1.647	2.026	2.979	3.796	4.257	-	5.273
	fr (%vol.)	0	1.04	1.29	1.90	2.43	2.73	-	3.39
	References	A0	A1	A2	A3	A4	A5	-	A7
PLA + 93A	fr (%wt)	–	–	1.87	2.61	3.14	3.28	4.54	4.88
	fr (%vol.)	–	–	1.25	1.75	2.11	2.20	3.06	3.29
	References	–	–	B2	B3	B4	B5	B6	B7