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Stiffness contribution of cellulose nanofibrils to composite materials

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ABSTRACT

Nanocomposites, reinforced by different types of cellulose fibrils, have gained increased interest the last years due to the promising mechanical properties. There is a lack of knowledge about the mechanical properties of the cellulose fibrils, and their contribution to the often claimed potential of the impressive mechanical performance of the nanocomposites. This paper investigates the contribution from different types of cellulose nanofibril to the overall elastic properties of composites. A multiscale model is proposed, that allows back-calculation of the elastic properties of the fibril from the macroscopic elastic properties of the composites. The different types of fibrils used were nanofibrillated cellulose from wood, bacterial cellulose nano-whiskers and microcrystalline cellulose. Based on the overall properties of the composite with an unaged polylactide matrix, the effective longitudinal Young's modulus of the fibrils was estimated to 65 GPa for the nanofibrillated cellulose, 61 GPa for the nano whiskers and only 38 GPa for the microcrystalline cellulose. The ranking and absolute values are in accordance with other studies on nanoscale morphology and stiffness estimates. Electron microscopy revealed that in the melt-processed cellulose nanofibril reinforced thermoplastics, the fibrils tended to agglomerate and form micrometer scale platelets, effectively forming a microcomposite and not a nanocomposite. This dispersion effect has to be addressed when developing models describing the structure–property relations for cellulose nanofibril composites.

1. Introduction

The majority of composites available today are made of petroleum-based polymers together with synthetic reinforcement fibers, e.g. carbon fiber, aramid fiber or glass fiber. However, the demand of renewable and biodegradable materials is rapidly increasing as the costumers get more aware of the environment. The focus of environmentally friendly composites has led to investigations of alternative constituents for composites. Example of renewable composites could be polylactide (PLA), poly hydroxybutyrate (PHB) or acid cellulose esters reinforced by natural fibers such as wood fibers or flax fibers (Oksman et al., 2003; Wong et al., 2004; Pilla et al., 2009). Such natural cellulose fibers typically have a diameter of 20 μm or more, and a length in the mm range. Prompted by the impressive property improvements of nanosized reinforcement, such as carbon nanotubes (e.g. Thostenson et al. (2001)) and exfoliated nanoclay (e.g. Lau et al. (2006)), there is currently a growing interest in renewable cellulose nanofibre reinforcement in composite materials. In particular for soft polymers matrix materials, e.g. in the rubbery state, considerable stiffness increases can be observed for small amounts of nanosized reinforcement compared with corresponding effects for microscale reinforcements (Papon et al., 2012). With a well-dispersed nanocomposite combining hard fillers and a soft binder, excellent mechanical properties can be achieved, which is also the case for nacre, bone and other biomaterials found in nature (Walther et al., 2010). In comparison to e.g. carbon nanotubes (Dzenis, 2008), cellulose nanofibrils have a functional surface, available for surface modifications to control the fibril–matrix interface and the dispersion of the fibrils in the polymer (Lönnberg et al., 2008). The abundance of hydroxyl groups on the surface cellulose fibrils facilitates interaction with polar matrix systems, and formation of a stiffening network (Rusli and Eichhorn, 2008). Examples of nanoscale cellulose reinforcement are nanofibrillated cellulose (NFC) and bacterial cellulose nano-whiskers (BC) (Siró and Plackett, 2010). Natural cellulose is often present as fibrils (bundles of aligned cellulose molecules) with a width of 10–20 nm and a length of several μm. These fibrils in turn are assembled into larger structures, e.g. plant fibers. By chemomechanical treatment of wood fibers it is possible to liberate the fibrils into so called nanofibrillated cellulose (NFC) (Pääkkö et al., 2007). The terminology for these fibrils with nanoscale lateral dimensions is still not consolidated as pointed out by Chinga-Carrasco (2011). Microfibrillated

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cellulose (MFC) refers to nanofibrils produced by fibrillation of wood pulp fibers and separation of the cell-wall microfibrils. NFC is used in this work to denote the all types of fibrils made from wood pulp. Another example of nanoscale cellulose reinforcement is bacterial cellulose nano-whiskers (BC) which are produced by a the bacteria *Acetobacter xylimum*, and can be found as one of the constituents in the Asian confectionary *Nata-de-coco* (Budhiono et al., 1999). These nano-whiskers have attracted attention due to its mechanical properties and ability to be used as reinforcement in polymers (Iguchi et al., 2000). Essentially, most research activities have been focused on the important and challenging tasks to manufacture cellulose-based nanocomposites with well-dispersed fibrils. Few studies have investigated the contribution of the potentially stiff nanofibrils to the stiffness of the macroscopic composite material. A deeper understanding of the reinforcing mechanisms could contribute to the development of improved mechanical performance of cellulose nanocomposites. The purpose of the present study is to use a suitable micromechanical model to determine the effective contribution of nanocellulose fibrils to the stiffness of the composite. Composite materials with cellulose contents of 10 wt% have been produced. Three different reinforcing elements were used: microcrystalline cellulose (MCC), bacterial cellulose nano whiskers (BC) or nanofibrillated cellulose (NFC). The fibrils were embedded in a matrix of poly(lactic acid), PLA, a renewable semi-crystalline thermoplastic. Effects of fibril type, degree of crystallinity of the polymer matrix and reinforcement dispersion are discussed.

2. Modelling

A mixed analytical–experimental method is proposed to determine the effective reinforcement stiffness from the composite stiffness. The model includes several parameters, e.g. inclusion shape, inclusion volume fraction, inclusion orientation distribution, elastic properties of the composite and elastic properties of the surrounding matrix and of the inclusions. The structure of the material is based on observed morphologies at high magnification using field-emission scanning electron microscopy. An example is shown in Fig. 1, in addition to micrographs presented in the results section below.

The multiscalar model presented in this paper relates the in-plane isotropic elastic properties of a composite based and the elastic properties of the nanoscale constituents. The model is composed of three dimensional laminate theory (Whitcomb and Noh, 2000), micromechanical model for statistically isotropic composites with arbitrary internal phase geometry by Hashin (1983) and a self-consistent Mori–Tanaka model (Mori and Tanaka, 1973). A schematic illustration of the working process is given in Fig. 2, showing how the elastic properties of the nano and microscale constituents are homogenized to determine the elastic properties of the macroscopic composite.

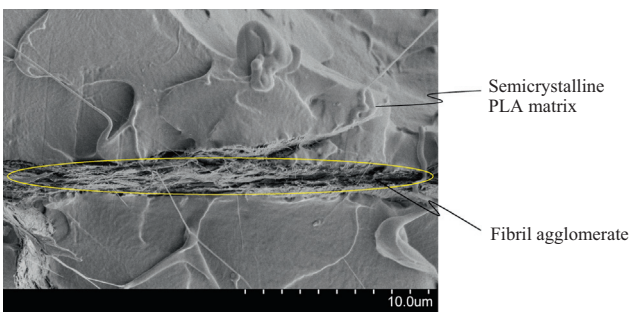

Fig. 1. Cross section of one of the composites reinforced by BC. The image shows a platelet of agglomerated BC imbedded in the matrix.

STEP I. The Young's modulus of a semicrystalline thermoplastic, consisting of crystallites embedded in the matrix in the amorphous state, can be expressed in terms of the elastic properties of the crystalline inclusions (i.e. $E_{m,c}$, $G_{m,c}$, $\nu_{m,c}$), the isotropic constants of the amorphous matrix ($E_{m,a}$, $G_{m,a}$, $\nu_{m,a}$), the volume fraction of the crystallites, $V_{m,c}$, and the volume fraction of the amorphous matrix materials, $V_{m,a}$. Any of the conventional elastic parameters for isotropic materials, i.e. Young's modulus, shear modulus, Poisson ratio and bulk modulus, can be expressed in terms of two other elastic parameters. Here, Hashin's micromechanical model for statistically isotropic composites with arbitrary internal phase geometry was used (Hashin, 1983) to express the properties of the semicrystalline thermoplastic. The model can also be used for particle reinforced composite materials. An exact solution of the moduli for such a material is not available, but relatively close upper and lower bounds for the moduli are given. For the bulk modulus of the semicrystalline matrix, K_m, the bounds are given by

$$K_{m(-)} = K_{m,a} + \frac{V_{m,c}}{\frac{1}{K_{m,c} - K_{m,a}} + \frac{3V_{m,a}}{3K_{m,a} + 4G_{m,a}}} \tag{1}$$

and

$$K_{m(+)} = K_{m,c} + \frac{V_{m,a}}{\frac{1}{K_{m,a} - K_{m,c}} + \frac{3V_{m,c}}{3K_{m,c} + 4G_{m,c}}} \tag{2}$$

where $K_{m,c}$ and $K_{m,a}$ are the bulk moduli for the crystalline inclusions and amorphous matrix, respectively. For the shear modulus, the bounds are given by

$$G_{m(-)} = G_{m,a} + \frac{V_{m,c}}{\frac{1}{G_{m,c} - G_{m,a}} + \frac{6V_{m,a}(K_{m,a} + 2G_{m,a})}{5G_{m,a}(3K_{m,a} + 4G_{m,a})}} \tag{3}$$

$$G_{m(+)} = G_{m,c} + \frac{V_{m,a}}{\frac{1}{G_{m,a} - G_{m,c}} + \frac{6V_{m,c}(K_{m,c} + 2G_{m,c})}{5G_{m,c}(3K_{m,c} + 4G_{m,c})}} \tag{4}$$

where $G_{m,c}$ and $G_{m,a}$ are the shear moduli for the crystalline inclusions and amorphous matrix, respectively.

By taking the average of the upper and lower bounds of the bulk and shear moduli separately, the elastic parameters of the semicrystalline polymer matrix can be estimated:

$$K_m = \frac{K_{m(-)} + K_{m(+)}}{2} \tag{5}$$

$$G_m = \frac{G_{m(-)} + G_{m(+)}}{2} \tag{6}$$

$$E_m = \frac{9K_mG_m}{3K_m + G_m} \tag{7}$$

When Eqs. (1)–(7) are used for semicrystalline polymers where the inclusions are aggregates of anisotropic crystals, the average isotropic elastic properties of the aggregates have to be determined first. For slow cooling and limited flow during processing, it can be assumed that the crystalline aggregates are effectively isotropic. Although the single crystals are anisotropic, the resulting property of crystalline aggregates is then isotropic, since it is assumed that the crystallites have a random orientation distribution in space. The overall isotropic properties of the crystallite aggregate can be estimated by calculating the Voigt and Reuss shear moduli and bulk moduli. These results are a theoretical upper and lower limit. By taking the average of the Voigt and Reuss moduli, an average isotropic Young's modulus can be estimated (Ravindran et al., 1998). For an orthotropic material the Voigt shear modulus, G_V, and bulk modulus, K_V, are given by