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Modeling of ceramic particles filled polymer–matrix nanocomposites

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Abstract

In this work, the mechanical properties of polymer matrix–ceramic fillers nanocomposites were investigated. A PCL (poly-caprolactone) matrix was reinforced with increasing amount of nano-sized silica particles in the range 1–2.5% by weight, and the resulting properties were determined as a function of reinforcement characteristics and volume fraction. In order to gain a deeper insight into the mechanical behaviour of such nanocomposites, a numerical model able to reproduce the peculiar composite features was set up. The study focussed on the effect of particles size and amount on the achieved increment in the overall stiffness. The computational approach revealed that a third phase, namely the interphase, has to be taken into account in the model in order to accurately reproduce the experimental results.

Keywords: A. Particle-reinforced composites; B. Mechanical properties; B. Modelling; C. Finite element analysis (FEA); Nanocomposite

1. Introduction

Poly-caprolactone is a biodegradable polymer which has been investigated for medical devices, drug delivery systems, and recently it has been considered as a candidate material for tissue engineering [1,2]. Moreover PCL is suitable for preparing degradable packaging [3]. However, the main disadvantages associated with PCL are its low melting temperature and, mainly, its low elastic modulus and abrasion resistance.

A traditional approach to improve properties of polymers is to add a second phase either in the form of fibres or particulate. In the past twenty years, several composites have been produced by adding to the polymer matrix micro-sized reinforcements. Recently, the scientific and industrial interest has been focused on the so-called nanocomposites, i.e., materials in which the secondary phase is nano-sized. In fact, such composites show enhanced performance compared to traditional ones. In particular, a great deal of attention has been devoted to bi-phase or multi-phase systems where inorganic nanometric fillers are added to the polymer. Such reinforcement, if well dispersed in the matrix, offers a larger specific surface area compared to usual fillers; thus, the potential of these system is that the interfacial interactions between the matrix and the particles can be enhanced, leading to an improvement of the properties of the material [4]. Some authors reported that even at very low filler volume content such as 1–5% a considerable improvement of the mechanical and tribological properties can be achieved [5]. In particular, several authors proved that ceramic and silica nanoparticles can effectively reinforce bulk polymers [e.g. [5,6]].

The aim of the present research is to improve polycaprolactone mechanical performance by reinforcing with silica spherical nanoparticles. In fact, the addition of silica nanoparticles is beneficial with respect to the

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demanded properties without preventing the usage in the biomedical field [7]. In a previous paper, PCL based nanocomposites reinforced with spherical SiO_2 nanoparticles were prepared and experimentally characterized [8]. A significant increase in the elastic properties was obtained if the inclusions were functionalised in order to promote the interfacial adhesion between the two constituents and to achieve a fine nanoparticles dispersion.

In this work, in order to gain a deeper understanding into the mechanical performance of such nanocomposites and into phenomena occurring at the nanoscale, a modelling approach closely related to the composite morphology is proposed.

In fact several authors pointed out the need for analytical and computational models able to reproduce the behaviour of complex and heterogeneous materials. This methodology can be very helpful for a complete investigation of nanocomposites: computational simulations which can predict the overall mechanical behaviour of the system are an effective tool for a reliable design of such materials. Even if there are several examples of analytical and numerical modelling for traditional micro-sized composites, in the field of nanocomposites several issues still need to be developed and addressed. However, the approaches reported in literature devoted to the investigation of nanocomposite systems cover different length scales, ranging from atomistic to continuum mechanics; which approach could be the most suitable one is still a discussed topic.

Atomistic simulations such as Molecular Dynamics (MD), although very accurate, cannot deal with very large time and length scales, which are typically involved in structural nanocomposites. On the other hand, at the nanoscale, analytical models are difficult to establish or too complicated to solve [9]; in fact, the analytical equations which are based on micromechanics and are widely utilized for traditional composites with micro-sized inclusions should be tested in order to validate their applicability at the nanoscale.

Some recent papers proved the applicability of the Finite Element Method (FEM) for modelling composites with a nanometric secondary phase. For example, Liu and Chen demonstrated the feasibility of the application of the FEM approach to carbon nanotube-based composites, by using a representative volume element (RVE) [9]. Other authors used finite element models in order to gain a deeper insight into the mechanical properties of nanostructured systems [e.g. [10–12]].

It is worth noting that these FEM-based models are often applied to the so called representative volume element, thus assuming that the microstructure of the composite can be reproduced by assembling a large number of such elements. However, this can be a serious limitation when dealing with complex and highly heterogeneous composites microstructures, such as randomly dispersed particulate systems. Therefore, an approach able to consider the actual microstructure morphology of the nanocomposite is useful in order to accurately predict the overall properties.

Thus, in this work, a computational tool able to map a composite microstructure onto a finite element mesh is adopted in order to construct models which accurately reproduce the composite morphology and characteristics. Since it is well known that the shape, the spatial arrangement, the volume fraction and above all the size of the nanoparticles play a major role in the resulting performance, this numerical approach enables to have a deeper insight into the mechanical behaviour of such materials. In particular, the microstructural features having a significant impact on the overall properties can be identified.

Thus, the aim of the present paper is to thoroughly investigate mechanical properties of the PCL-silica nanocomposites. In particular, the computational model will be used to interpret the available experimental results [8], focussing on the fundamental mechanisms arising in such systems.

2. Materials and methods

PCL-SiO_2 nanocomposites were prepared by adding nanoparticles in the amount of 1% and 2.5% by weight, respectively.

The details of nanocomposites preparation are reported elsewhere [8] and here are only briefly summarized. The silica particles, with a spherical shape and a size in the range 100–200 nm, were functionalised by grafting a hydroxyl end-capped PCL in order to achieve a fine particulate dispersion and to improve the polymeric matrix–inorganic nanofiller interfacial adhesion.

Moreover, PCL based nanocomposites filled with neat silica nanopowders were prepared for comparison, to effectively evaluate the beneficial effect of the functionalisation.

SEM observation of fracture surfaces allowed the investigation of the SiO_2 nanoparticles dispersion and the PCL/nanoparticles interfacial adhesion. An example of the nanocomposite microstructure is reported in Fig. 1. As can be seen from the image, the silica fillers are evenly distributed into the matrix and the bond between the two phases appears strong.

The mechanical properties of the so obtained nanocomposites were evaluated by tensile tests using an Instron machine.

Starting from nanocomposites microstructures such as Fig. 1, computational models for the different nanocomposites were prepared by using the computational code OOF [13,14]. OOF is an innovative finite element tool: in fact, by using its pre-processor, digitised images such as SEM micrographs can be easily mapped onto