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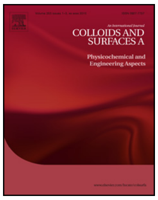

Nanocomposites based on epoxy resin. Simulation of microindentation process

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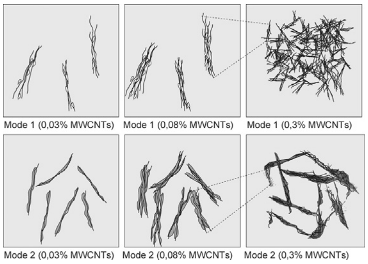
HIGHLIGHTS

- Microindentation experiments of nanocomposites based on epoxy resin were realized.
- Positron annihilation lifetime spectroscopy determined structural peculiarities.
- The microindentation process was simulated by means of finite-element method.
- Dependence of yield strength from concentration of carbon nanotubes was determined.
- The distribution of Von Mises stress and plastic strain under indenter was shown.

GRAPHICAL ABSTRACT



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ABSTRACT

The process of microindentation of nanocomposites based on epoxy resin was simulated numerically by means of finite-element method (FEM). Literature data for yield strength, tensile strength, elongation and Poisson's ratio of epoxy resin were used as initial values for numerical simulations. Numerical results obtained by means of finite-element simulations were then compared with experimental results, obtained by means of microindentation. The distribution of equivalent Von Mises stress in investigated materials during the process of microindentation, as well as the distribution of the equivalent plastic strain after unloading were determined. Conclusions about influence of interface interactions have been made by combining the results obtained from microindentation and positron annihilation lifetime spectroscopy.

1. Introduction

Epoxy resin/carbon nanotubes nanocomposites are class of engineering materials with high technological interest because of their very good mechanical properties, thermal and electrical conductivity, due to enhancing role of the reinforced filler. Conventional theories explaining the effect of filler on mechanical properties as well as the additive low for microhardness are not applicable to CNTs composites. The high enhancement of mechanical properties of nanocomposites is mainly attributed to uniform dispersion of the filler and to the interaction between them and the matrix material. The interphase is a transition region between the nanofillers and the matrix with high value of the reactive

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surface area per unit volume of nanofillers. During last 10–15 years many reports published on these materials focus on investigation of the polymer matrix [1–3] and its interaction with carbon nanotubes. Most of efforts were oriented to surface functionalization of CNTs aiming better dispersion and better interfacial adhesion between CNTs and epoxy matrix. However, by now there is not unifying theory of optimal conditions for composition preparing and for a better interaction between the epoxy resin and carbon nanotubes. There are many factors influencing the properties of the final composite. For example Ci and Bai [4] investigated matrix viscosity, curing agent and curing condition. Volume fraction content of CNTs was investigated by Zhang et al. [5]. Rumera et al. [6] investigated type and dimensions of carbon nanotubes and their aspect ratio (length/diameter) was investigated by Perez et al. [7]. Ganguli et al. [8] investigated their surface modification. Their orientation and alignment or entanglement and tend to agglomeration were investigated by Camponeschi et al. [9] and Wang et al. [10]. Different methods for the preparation of composites with good exfoliation of the filler based on sonication, stirring and calendering have been proposed by Zhang [5], Park [11], Sandler [12] and Gojny [13]. Pillai and Sinha Ray [14] have provided a comprehensive review, historical and thematic systematization of all publication on epoxy resin/carbon nanotubes nanocomposites containing over 200 references. Tribological behavior of polymers was reviewed by Myshkin et al. [15] since the mid-20th century to the present day.

Investigation of mechanical properties using depth-sensing indentation (DSI) [16] or scratch test [17] recently is widely used for study the material behavior of different materials. Being in close relation with both macromechanical characteristics and structural peculiarities, microindentation characteristics give some other aspects of material evaluation, so they could be considered as a link between macro- and micro-properties. Combined with positron annihilation lifetime (PAL) technique, another non-destructive technique, DSI allows going more inside in study the relation between structure and mechanical properties. For more comprehensive understanding of mechanisms of changes of the mechanical properties with nanofilling, the experimental characterizing is complemented with computer modeling and simulation of the indentation process. Both approaches are considered from Hu et al. [18] as a two wings in understanding the mechanisms of matrix–nanofiller interactions. Numerical methods can determine some properties or parameters that usually are difficult to obtain from experiments as well as gives information about the zones of deformations and stress under the indenter. They can also provide suggestions and give a guide for future experiments. 2D finite element modeling (FEM), is appropriate simulation for nanocomposites [18] and has been extensively used from Dong [19], Cannillo [20] and Avella [21]. Another possible approach which was demonstrated from Brostow et al. [22] is molecular dynamics computer simulations of scratch testing. The aim of present article is to illustrate how microindentation measurements are sensitive to the dispersion level and to distinguishing the good and bad dispersion of the MWCNTs in epoxy resin. It also aims to demonstrate how only on the base of two nondestructive methods (DSI and PAL technique) it is possible to obtain information about the structure of rather complicated polymer nanocomposites.

2. Experimental

2.1. Materials

Investigated nanocomposites consist from epoxy resin and carbon nanotubes. The nanocomposite matrix is D.E.R.TM 321 (ortho-cresyl glycidyl ether diluted standard bisphenol A based liquid epoxy resin), produced by Dow Chemical Company. The curing agent is polyethylene polyamine (PEPA), produced by Bakelite Co. The multiwall carbon nanotubes (MWCNTs) with external diameter 30 ± 10 nm and approximate length 10–20 μm are used. Two different processing modes were applied:

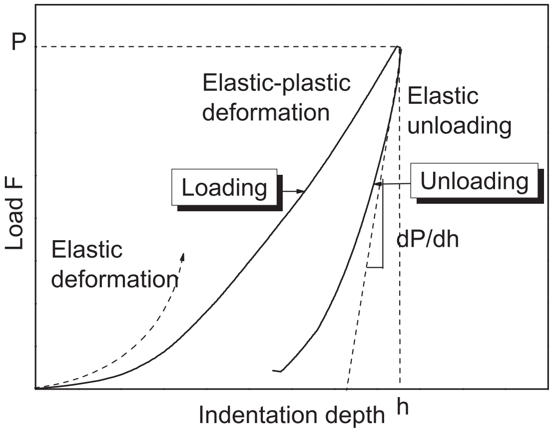

Fig. 1. Typical load–displacement curve.

- Mode 1 – MWCNTs dispersions in epoxy resin were prepared and then mixed with hardener PEPA in ratio 70:30.
- Mode 2 – MWCNTs were mixed directly with PEPA by high speed mechanical stirring and intensive ultrasonication and further the certain amount of epoxy resin was added for obtaining the desirable ratio. So MWCNTs surface is functionalized by amine groups of the hardener, thus improving chemical interactions with epoxy resin matrix at the interfaces during curing.

2.2. Investigation methods

2.2.1. Microindentation measurements

The measurements were performed on a Dynamic Ultra Micro Hardness Tester DUH-211S from Shimatzu Japan according to standard (ISO 14577-1). The method is known as a depth-sensing indentation (DSI) or instrumented indentation testing (IIT). One typical load-displacement curve is shown in Fig. 1. The loading part of indentation cycle may consist of an initial elastic contact, followed by plastic flow, or yield, within the specimen at higher loads. For viscoelastic materials the relationship between load and depth of penetration is not linear. We had the following test conditions:

- The test type is loading–unloading;
- The indenter is Vickers pyramid;
- Loading speed – 14 mN/s;
- Maximum force P – 200 mN;
- All measurements were performed at room temperature.

The following microhardness characteristics were measured during microindentation experiment:

- Dynamic hardness (DH) [23]:

$$DH = \frac{aF}{h^2}, \tag{1}$$

where (F) is the value of the instant load, a is a constant, h is a indentation depth. In the experimental part we mark with DH the hardness calculated under maximum applied load (P), respectively maximum indentation depth.

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