MEASUREMENT OF MECHANICAL PROPERTIES OF COMPOSITE MATERIALS

VILMA BURŠÍKOVÁ[a], ZUZANA KUČEROVÁ[a], LENKA ZAJÍČKOVÁ[a], ONDŘEJ JAŠEK[a], VÍT KUDRLE[a], JIŘINA MATĚJKOVÁ[b], and PETR SYNEK[a]

[a] *Department of Physical Electronics, Masaryk University, Kotlářská 2, 611 37 Brno,* [b] *Institute of Scientific Instruments, Academy of Sciences of the Czech Republic, Královopolská 147/62, 612 64 Brno, Czech Republic*
vilmab@physics.muni.cz

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1. Introduction

Composite materials or composites are multiple-phase materials that exhibit a significant proportion of the properties of all constituent phases such that a better combination of properties is realized. Those phases must be chemically and physically dissimilar and separated by a distinct interface. There are two categories of constituent materials: the matrix and the reinforcement or the dispersed phase. In a composite, at least one portion of each kind is required. The properties of composites are a function of the properties of the constituent phases, their relative amounts and the geometry of the disperse phase (i.e. the shape of the particles, the particle size distribution and orientation).

2. Nanocomposites

In contrast to conventional composites, where the reinforcement is on the order of microns, nanocomposites are reinforced with filler with at least one dimension that is less than 100 nm. Although some nanofilled composite have been used for more than 100 years (e.g. carbon black or fumed silica filled[1,2]), the discovery of carbon nanotubes become a new great challenge for nanocomposite research and industry. According to[3], six following characteristics distinguish the nanocomposite from the classic filled systems: particle-particle correlation (orientation and position) arising at low volume fractions (<0.001); large number density of particles per particle volume (106–108 particles/μm^3); extensive interfacial area per volume of particles (103–104 $m^2\,ml^{-1}$); short distances between particles (10–50 nm at 1.8 vol.%); comparable size scales among the rigid nanoparticle inclusion, distance between particles and the relaxation volume of the polymer chains.

The interfacial region has different properties than the bulk material because of its proximity to the surface of the filler. Nominally, the spatial extent of this perturbed matrix is thought to extend into the bulk one to four times the radius of gyration of the matrix, Rg, which has a value of around tens of nanometers. Because of the increased number of particles, the distance between particles in the nano-filled system is comparable to the size of the interfacial region (10 nm). Thus, the relative volume fraction of interfacial material to bulk is drastically increased. This implies a necessity to optimize the properties of the interfacial region in nanocomposites. On the other hand, this region is a source of many potentially novel properties of nanocomposites derived from the interface. It can influence the mechanical properties of the nanocomposites as well as their conductivity and percolation behavior.

The final microstructure and properties of the carbon nanotubes (CNT)-based polymer composite will depend on how the CNTs will distribute, disperse and orient. The CNT orientation state determines the anisotropic functionality. Properties of composites are significantly better, if CNTs are oriented in one direction, than if they are oriented randomly[4,5]. Another challenge in fabrication of the CNT-based polymer composites is the homogeneous dispersion of the CNTs in the polymer matrix so that it has uniform properties and can efficiently handle load transfer during structural excitation[4,6,7]. It is a significant challenge in fabrication of the CNT-based polymer composites because the CNTs, in their manufactured state, cluster together in any suspension due to strong Van der Waals forces. Many techniques such as application of ultrasonic bath or chemical modification of the CNT surface have been attempted to separate and disperse CNTs in polymer resins to various degree of success[4,8–10]. There are four important parameters that will describe the suspension characteristics: CNT dispersion, concentration, aspect ratio and orientation[11]. The importance of dispersion and orientation of CNTs is obvious from the above paragraph. The CNT concentration and aspect ratio determine how easily CNTs can move and interact with each other to build interconnecting network which can transfer heat and electrons. There are three general ways of dispersing nanofillers in polymers. The first way is direct mixing of the polymer and the nanoparticles either as discrete phases or in solution. The second way is *in-situ* polymerization in the presence of nanoparticles and the third is *in-situ* formation and *in-situ* polymerization. These are so-called hybrid composites[12].

Carbon nanotubes are increasingly being used in nanocomposite preparation as a filler of many different matrices, ceramics, metal, polymer and also in clay-polymer composites[13–16]. With their high strength, high modulus, light weight and high aspect ratio they seem to be ideal filler. However, they are held in bundles a do not disperse easily, they are inert with low wettability and that hinders their full utilization as a filler. It has already been reported that functionalization of CNTs greatly improves their dispersion in a matrix and consequently the properties of the composite[17]. In this work the preparation of the polyurethane (hereafter PU) composite with nanotubes is described. Both unmodified and modified multi-

walled CNTs (hereafter MWCNTs) were used. The structure and properties of composite with both kinds of filler are compared. The functionalization of MWCNTs in inductively coupled plasma ICP is also reported.

3. Mechanical properties of the composites

There are several basic problems associated with the determination of the mechanical properties of composite film consisting of hard particles and viscoelastic-plastic matrix. The evaluation of material parameters such as elastic modulus and plastic hardness of the viscoelastic-plastic film is problematic because these materials exhibit also a significant time dependent plastic deformation (creep). If we load such system to a maximum load and then keep penetration depth constant, the load will relax under some plastic or viscoelastic response (anelastic – time dependent plastic deformation). Two different indentation methods were used to study the mechanical properties of the composites.

A Fischercope H100 depth sensing indentation (DSI) tester was used to study the indentation response of composites on glass substrates. Several different testing conditions were used in order to find the optimum procedure allowing the suppression of the influence of the time dependent indentation response of CNT-filled PU composite on a glass substrate. The loading period of 20 s was followed by a hold time of 20 s or 60 s, an unloading period of 20, 5 or 1 s and finished after holding the minimum load for 20 or 60 s. The tests were made for several different indentation loads in order to study the composite mechanical properties of the film/ substrate system from near surface up to film-substrate interface. The applied load varied from 1 to 1000 mN. An example of the time dependence of the load is shown in Fig. 1.

In the case of the second, dynamic method, the CSM ultrananoindenter (UNHT) was used. The indentation measurement was based on the application of an oscillating force superimposed to the increasing indentation load in which the transfer function between the load and indentation depth provides a method of calculating storage and loss modulus of the material.

The PU-CNT nanocomposite preparation was as follows. Appropriate amounts of CNTs, polyol, diluter and antistatic agent were weighted out, stirred well manually, glass balls ensuring the mechanical perturbance were added and the whole mixture was ultrasonicated for 60 minutes. Than isocyanate was added and the mixture was stirred once more. After that it was poured onto glass substrate surrounded by the frame. Liquid in the frame created a flat level and let dried at the laboratory temperature. After 48 hours the composite was dry enough to be removed from the frame. The chemicals weight rate was 7 : 2 : 1 (polyol : isokyanate : diluter) and the CNT concentration in composites was 0.1 wt%.

4. Results

In Fig. 1 the testing conditions (dependence of the applied load on the time) used and the corresponding time dependences of the indentation depth are illustrated for several studied samples.

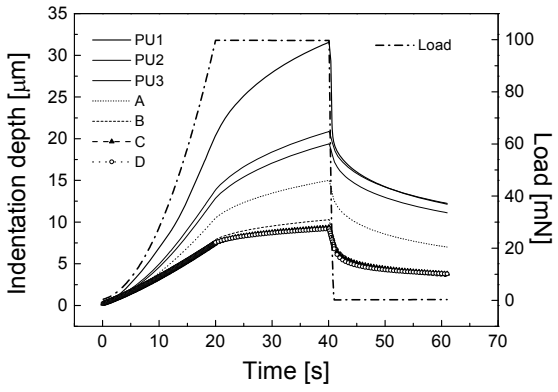

Fig. 1. **Comparison of the time dependence of the load with the time dependence of the indentation depth for 3 different types of polyurethane matrices PU1-PU3 and four composites marked A,B,C,D, reinforced by CNTs**

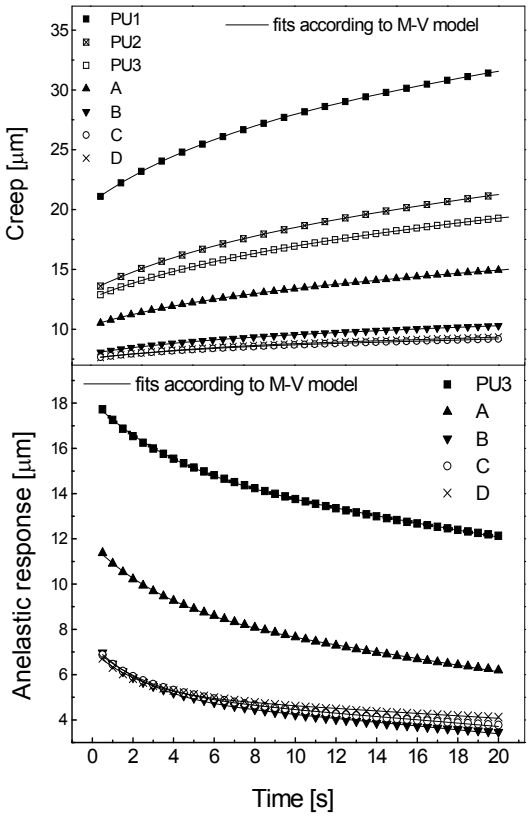

Fig. 2. **Experimental indentation creep and relaxation data fitted with Maxwell-Voigth (M-V) reological model obtained for pure PU samples and PU-CNT nanocomposites**

The mechanical properties of PU depend substantially on its preparation conditions, it is well-known that the composition of PU can be varied to produce hard and stiff to soft and rubbery materials. In Fig. 1, the indentation responses of three different PU coatings to the applied load change in time are shown. The substrate material was glass. Using the indentation study, we have found that mechanical properties of PU coatings depend not only on the preparation mixture, but also on the amount of chemicals used for the preparation, i.e. they are dependent on the coating thickness. Probably it is caused by different solidification process at the surface, which is in contact with air and in the bulk of the material. In case of the sample PU1, which was thicker than 300 μm, there was a harder skin at the surface and the hardness in the bulk decreased of one order of magnitude. In case of samples PU2 and PU3 with thicknesses lower than 300 μm the solidification process was more homogeneous, and the differences in surface and bulk properties are less. The hardness of the most thin and stiff PU matrix P3 was 22 MPa, its indentation modulus E_{IT} was 1.14 GPa, the loss modulus E_L was 0.15 GPa.

The PU matrix was in each case softer than the multiwall carbon nanotube (MWCNT) containing PU (samples A,B,C,D) and showed more significant indentation creep. The unloading cycle showed for PU coatings sudden rush decrease in indentation depth. The composite film A consisting of nonmodified nanotubes in polyurethane matrix exhibited slightly higher resistance against indentation compared to P3. However, the COOH activated carbon nanotubes in case of sample B (0.05 % of MWCNT) and sample C (0.1 % of MWCNT) substantially improved the PU matrix properties. The COOH functionalisation of MWCNTs increased the composite resistance against indentation and creep and resulted in better relaxation (anelastic response) ability (see Fig. 1 and Fig. 2). The homogeneity of the composite was improved from the point of view of the indentation test and the scatter in measured values decreased. The activation of the carbon nanotubes improved the hardness and the elastic modulus of the prepared samples. These results were proven also by dynamic mechanical analysis. Results on the depth dependence of the hardness and elastic modulus are shown in Fig. 3, it is obvious, that the functionalised CNTs offer much better mechanical properties.

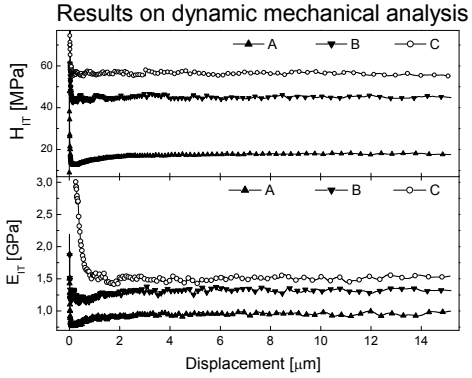

Fig. 3. **Dependence of the hardness and the elastic modulus on the indentation depth for nanocomposites A, B and C;** A – nanocomposite consisting of nonmodified nanotubes in PU matrix, B – COOH activated carbon nanotubes – 0.05 % of MWCNT, C – COOH activated carbon nanotubes – 0.1 % of MWCNT

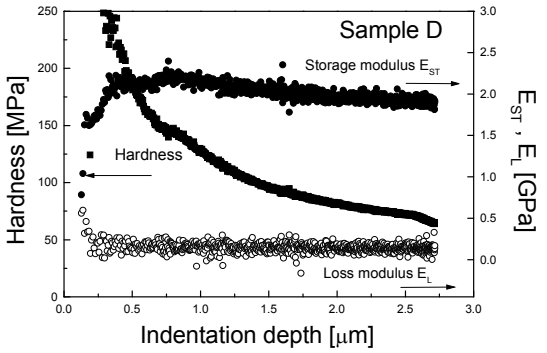

Fig. 4. **Results on dynamic mechanical analysis of nanocomposite sample D.** Dependence of the hardness, storage and loss modulus, E_{ST} and E_L on the indentation depth for nanocomposite D. D – nanocomposite consisting of plasma modified carbon nanotubes in PU matrix – 0.1 % of MWCNT

In case of sample D (0.1 % of MWCNT), the capacitively coupled low pressure glow discharge was used to activate the MWCNT fillers. The MWCNTs were treated with r.f. power 15 W of at the frequency of 13.56 MHz in mixture of oxygen and argon. From Fig. 1 and Fig. 2 it is evident, that the effect of this treatment on the properties of the PU/CNT composite is of the same quality as in case of commercial COOH treated CNTs.

In Fig. 4 the viscoelastic properties of composite filled with plasma modified CNTs (sample D) are characterised using dynamic mechanical analysis. The hardness of sample determined using this analysis was 65 MPa, the storage modulus E_{ST} was 1.95 GPa, the loss modulus E_L was 0.12 GPa and the loss factor φ was 2.8°. An increase in the hardness approaching the surface region was observed in each case of prepared coatings.

Moreover, we analysed the time dependent mechanical properties of the prepared coatings using several mechanical models (Kelvin-Voigt, Voigt, Maxwell-Voigt) The four-element Maxwell-Voigt model was found to be the most suitable approach to describe the time-dependent behaviour of the prepared coatings as it is shown in Fig. 2. In this model, the material response is described by serial combination of Maxwell model and Kelvin-Voigt model.

5. Conclusion

Complex mechanical characterization of MWCNT/PU composites was done. Four types of coatings were compared. The coating with commercial pure MWCNT filler exhibited viscoelastic properties as the PU matrix, but its mechanical

properties such as hardness, elastic modulus and creep resistance were slightly improved. Two different concentrations of MWCNTs commercially functionalized with COOH group were studied. These composites showed improved mechanical properties, and the modified nanotubes proved to be much better fillers than the unmodified MWCNTs due to stronger filler-to-matrix attachment. Because the modified nanotubes seem to be much more convenient composite filler, the first experiments with nanotube modification have been carried out. Modification using inductively coupled discharge in argon and oxygen mixture was successful and the mechanical properties of the composite were increased at the same level as in case of the commercially COOH functionalized MWCNT fillers.

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V. Buršíková[a], Z. Kučerová[a], L. Zajíčková[a], O. Jašek[a], V. Kudrle[a], J. Matějková[b], and P. Synek (*[a]Department of Physical Electronics, Masaryk University, Brno, Czech Republic, [b]Institute of Scientific Instruments, Academy of Sciences of the Czech Republic, Brno, Czech Republic):* **Measurement of mechanical properties of composite materials**

The aim of the present work was the study of mechanical properties of MWCNT/PU. Four types of coatings were compared. Two different concentrations of MWCNTs commercially functionalized with COOH group were prepared and studied. These composites showed improved mechanical properties compared to PU, and the modified nanotubes proved to be much better fillers than the unmodified MWCNTs due to stronger filler-to-matrix attachment. Because the modified nanotubes seem to be much more convenient composite filler, the first experiments with nanotube modification have been carried out. Modification using inductively coupled discharge in argon and oxygen mixture was successful and the mechanical properties of the composite were increased at the same level as in case of the commercially COOH functionalized MWCNT fillers.