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Short communication: Material properties

Hybrid cyanate ester resin-based nanocomposites: Increased indentation size effect due to anomalous composition of micron subsurface layer

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ABSTRACT

Hardness of materials increases with decreasing indentation depth from macro-to nano-scales, which is known as the indentation size effect (ISE). This effect has been associated with indenter shape, frictional forces, dislocation models and other features. We show an anomalously high ISE for a 1-μm subsurface layer in the hybrid nanocomposites based on densely cross-linked Cyanate Ester Resins (CER) containing functionalized 3-D POSS or 2-D MMT nanoparticles (NP). This effect disappears after mechanical stripping of the surface layer. Energy dispersive X-ray (EDX) spectral analysis shows that this anomaly was caused by increased content of NP (Si and Al elements), by 2.5 times, in the 1-μm subsurface layer. The hardness of the 1-μm subsurface layer in these brittle nanocomposites is due to its peculiar composition, and must be taken into account when considering mechanical strength and frictional properties.

1. Introduction

Depth-sensing indentation (DSI) represents one of the principal techniques for the mechanical characterization of materials. At the present time, DSI instruments can produce indentations with depths from a few tens of nanometers to a few microns. This range of indentations is, respectively, termed as nano-, submicro- and microindentation. Recent articles [1–3] have reviewed numerous contributions to DSI for polymers and polymer nanocomposites. A variation of hardness H and indentation modulus E_i as a function of indentation depth h has been reported for DSI in some studies. As a rule, an increase of these mechanical characteristics with decreasing indentation depth has been observed, especially in nano- and submicroindentation experiments. This observation is known as the indentation size effect (ISE) and has been extensively investigated. ISE has been observed for the indentation of vastly different material types including very soft [4], soft or semi-hard polymeric materials [2,3,5–7], polymer nanocomposites [1,8] and very hard solids [2,9].

The ISE has been attributed to diverse sources, the most common ones are: (a) the indenter-sample contact, and (b) mechanisms associated with the material deformation. The shape of the indenter and tip imperfection has turned out to be crucial for nano- and microhardness estimation. A large number of studies report substantial ISE that is explained in terms of instrumental considerations such as tip blunting, frictional forces between the indenter and sample, etc. [10–13], that may disappear, for example, when using a different indenter tip [7]. A number of models have been proposed based on strain gradient plasticity to explain the hardness increase with decreasing indentation depth [1–3]. Authors [14] have considered the apparent enhanced stiffness of amorphous polymer surface as a result of confinement effects under localized contact load, and it has been associated also with Frank elasticity [12].

On the other hand, there are researchers that explain ISE through polymer properties. For example, it has been shown that: polymers containing aromatic rings in their molecular structure exhibited ISE above the micron length scale, whereas for polymers without these rings the ISE starts at smaller indentation depths or it is not present at all [15]. Of course, in some cases such factors as surface oxidation, ageing or modification of the near-to-surface layers of polymers during fabrication, or the higher degrees of

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crystallinity at the near-surface region could also result in enhanced ISE.

Little work has been devoted to the correlation between nano-, submicro- and micro-indentation results and structural information that can be extracted by other techniques. This is an area that still needs to be developed and represents one of the most attractive challenges in polymer nanocomposites and materials science [1].

One of the most important classes of modern high performance polymeric materials is densely cross-linked Cyanate Ester Resins (CER). CER (polycynurates) have a unique complex of physical properties including thermal stability up to 400 °C, glass transition temperatures in the range of 250–400 °C, good fire, radiation and chemical resistance, low water absorption, high adhesion to different substrates and excellent dielectric properties [16,17]. As a result, CER are widely used for producing high temperature structural or functional materials in aerospace and microelectronics. Additionally, their properties may be enhanced by forming them into nanocomposites [18,19], in particular at ultralow and low NP contents [20–23]. In this work, a combination of indentation measurements and energy dispersive X-ray (EDX) spectral analysis of subsurface layers is used in hybrid nanocomposites based on densely cross-linked CER (polycyanurate) that revealed an anomalously increased NP content contributing to increased hardness (high ISE) for a 1-μm subsurface layer.

2. Experimental

2.1. Materials

2,2′-bis(4-cyanatophenyl)isopropypidene (dicyanate ester of bisphenol A (DCBA)), under the trade name PRIMASET™ BADCY kindly supplied by Lonza (Switzerland), was used as CER monomer. The mixture of cobalt acetyl acetonate (0.017 phr) and nonylphenol (2 phr) was used as a catalyst for CER polymerization. 3-D epoxy cyclohexyl-functionalized polyhedral oligomeric silsesquioxane (ECH-POSS, POSS® Cage Mixture from Hybrid Plastics Inc., Hattiesburg, MS, USA) and 2-D amino-modified montmorillonite (amino-MMT clay, under trade name Nanomer® I.31PS from Nanocor Inc., USA) were used as nanoparticles. The hybrid CER-based nanocomposites containing 2.5 wt% of ECH-POSS or amino-MMT, with T_g = 294° and 279 °C (DSC), respectively, were synthesized. The initial CER/NP mixtures were first stirred at 170 °C for 2 h for prepolymerization of monomer and chemical grafting of NP to the growing CER network (their hybridization) through the reaction between cyanate and epoxy or amino groups. Then, the heating was stopped, and the mixtures were cooled down to 25 °C. After that, the catalyst was added, mixed, and the mixtures obtained were poured into a PTFE-coated mold and cured over the temperature range from 25° to 300 °C with heating rate of 0.5 °C/min. The chemical structure of the nanocomposites obtained has been previously confirmed by FTIR spectroscopy [20–23].

2.2. Techniques

Microhardness of the nanocomposites was determined under different loads by means of indentation with a Vickers pyramid (microhardness testing PMT-3 instrument, LOMO, Russia), at a loading time of 10 s. Microhardness was calculated by the formula: $H = 1854\,P/d^2$ where H is microhardness (GPa), P is load (N) and d is indent diagonal (μm).

Elemental analysis of subsurface layers was performed by means of an Oxford Instruments INCA energy dispersive X-ray (EDX) spectrometer at operating voltages of 3, 5 and 15 kV that provided the analysis of about 1, 1.5 and 3 μm thick subsurface layers, respectively. Comparative estimation of nanoparticle contents within the above layers was performed by the determination of Si (for ECH-POSS) and Si and Al (for amino-MMT) contents; C, N and O contents were also determined.

Analysis was performed for the initial, untreated surface and after its treatment by stripping a ~50 μm thick surface layer by means of mechanical grinding and polishing. The average values of element contents were determined from five EDX spectra (repeat measurements) in each case.

3. Results and discussion

Fig. 1(a, b, c) shows microhardness H versus indentation depth h plots for neat CER matrix and two CER-based nanocomposites. The

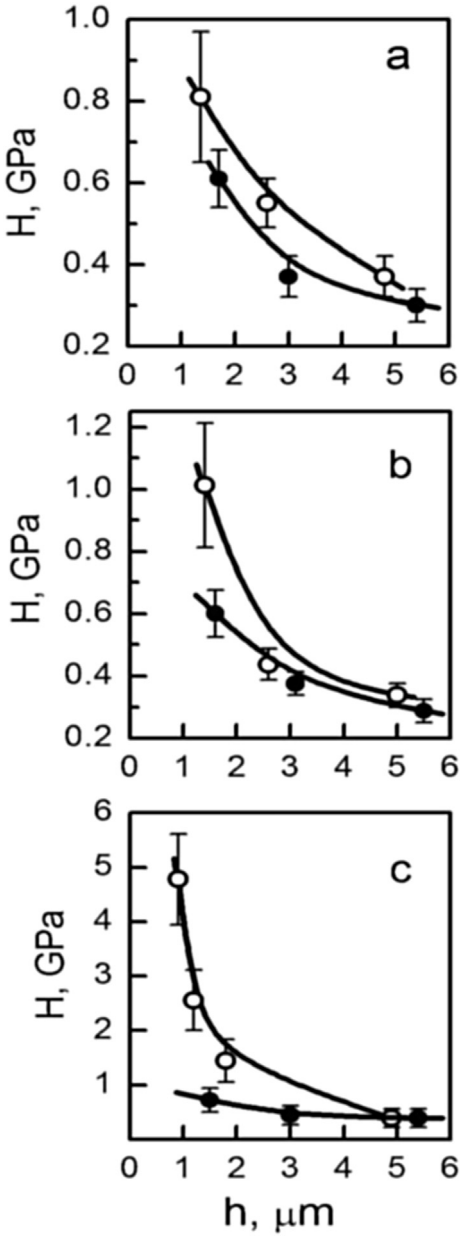

Fig. 1. Microhardness of neat CER matrix (a) and the CER-based nanocomposites with 2.5 wt% of 3-D ECH-POSS nanoparticles (b) or 2-D amino-MMT nanoparticles (c) as a function of indentation depth. White circles indicate the initial untreated surface, and black circles indicate values after mechanical grinding and polishing.