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SCIENCE DIRECT
Polymer Testing 25 (2006) 443–451
POLYMER TESTING
www.elsevier.com/locate/polytest

Test Method

Atomic force acoustic microscopy analysis of epoxy–silica nanocomposites

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Received 6 December 2005; accepted 16 January 2006

Abstract

A DGEBA-based epoxy matrix was loaded with 10, 20 and 30 phr of fumed silica particles. Single edge notched bend (SENB) specimens were prepared and deformed to failure in three-point bending configuration. Their fracture surfaces were examined by atomic force acoustic microscopy (AFaM) in order to obtain information about the local elastic modulus of the surface at high spatial resolution. The collected information was correlated to the bulk thermo-mechanical properties of the composites. In particular, the decrease in thermo-mechanical properties like tensile modulus, yield strength, stress at break and glass transition temperature, observed for samples filled with 10 and 20 phr with respect to the unfilled matrix was found to correspond to highly heterogeneous fracture surfaces presenting a broad distribution of elastic modulus values. The AFaM data were interpreted as representative of different degrees of filler exposure on fracture surfaces and also of localized cavitation effects involved in crack propagation, both phenomena accounting for the effective plasticizing effect macroscopically observed at silica amounts of 10 and 20 phr. A substantial reduction in the exposure probability of silica particles on fracture surfaces was found for the sample filled with 30 phr of silica, which also displayed an improvement of the mechanical and thermal properties. This latter evidence was tentatively explained by supposing a physical immobilization of polymer chains at the polymer-matrix interface.

Keywords: Elastic modulus; Epoxy; Silica; Nanocomposites; Atomic force microscopy; Acoustic modality

1. Introduction

In recent years, great attention has been focused on polymeric nanocomposites, especially those obtained from layered silicates [1,2] dispersed in thermoplastic and thermosetting matrices. If properly dispersed, these fillers can substantially improve the properties of the resulting nanocomposites with respect to conventional microcomposites loaded with the same amount of filler. In fact, the properties of the polymeric matrices can be substantially altered by the interactions with a nano-filler. The main reason for this behavior has been identified in the much higher interfacial area between matrix and filler in nanocomposites than in conventional microcomposites [1,2]. As a consequence, the macroscopic behavior of the nanocomposites cannot be accurately predicted by the rules proposed for microcomposites [3] and sometimes unexpected

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0142-9418/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymertesting.2006.01.009

effects can be observed in thermal [4–6] and mechanical properties.

The availability of a wide range of operative techniques in atomic force microscopy (AFM) [7] allows one to carefully control the degree of sample-probe interaction while preserving sample integrity. This is one of the reasons why AFM has been widely used to analyze non-conductive samples, especially in those cases where any substrate preparation could potentially alter the observed microstructure or when the required resolution level was critical [8–10]. Moreover, the analysis of direct contact force with the substrate allows one to obtain information on the mechanical response of highly localized portions of a given microstructure. In this way, it is possible to have almost direct access to microscopic quantities otherwise only derivable from theoretical, or even phenomenological, models [11–14] based on macroscopic average values.

In the present work we focus our attention on the use of atomic force acoustic microscopy (AFaM) for the analysis of fracture surfaces of epoxy-based silica-nanocomposites in an attempt to correlate their sub-micrometric structure, as revealed by the distribution of local elastic modulus, to their macroscopic thermo-mechanical behavior. That behavior has been extensively investigated by this research group and described in a companion paper [15]. Unlike previous works concerning polymeric composites, which emphasized the imaging capabilities of the AFM techniques, we focused our attention on the possibility of gaining numerical information characterizing the physical appearance of the fractured surfaces, analyzed to correlate them with the bulk thermo-mechanical properties already measured. The acoustic mode (AFaM) was selected to exploit the higher stiffness which is exhibited by a viscoelastic material at the ultrasonic frequencies used to perform measurements, since previous works reported on the difficulties of determining elastic characteristic in polymeric nanocomposites by "static" force-distance spectroscopy [16]. Moreover, the choice of AFaM technique to investigate the fracture surface was prompted by the high spatial resolution required to recognize structural heterogeneity on sub-micrometric scale in nanocomposites. In fact, scanning electron microscopy techniques like backscattered electrons (BSE) imaging or energy dispersion X-Ray spectroscopy (EDXS) are sensitive to compositional differences but lack the required lateral and in depth resolutions. This can be easily recognized just considering that typical penetration depth of BSE analysis is about 200 nm and that one of EDXS is as high as 500 nm (depending on sample and operative conditions), while AFaM spectroscopy sampling depth in our case was estimated to be less than 25 nm.

2. Experimental section

The selected epoxy matrix was a commercial bicomponent system (EC57/K63), supplied by Camattini S.p.A. (Collecchio, Parma, Italy), consisting of a DGEBA-based low molecular weight epoxy resin (EC57: epoxy-equivalent 172–182 g/eq) and a polyamide–amine curing agent (K63: 88–91 g/eq). The filler was the Cab-O-Sil M5 fumed silica, supplied by Cabot GmbH (Hanau, Germany), consisting of nanometric particles of untreated pure amorphous silica with nominal surface area of about 200 m^2/g. Composite samples conforming to UNI EN ISO 527 type 1BA dumb-bell geometry were prepared with filler loadings of 10, 20 and 30 phr (corresponding to 6.3, 11.8 and 16.7 percent by weight and to 3.3, 6.4 and 9.2 percent by volume, respectively) by a solvent assisted dispersion procedure accurately described in a companion paper [15]. Samples for three-point bending tests were machined from the central part of dumb-bell test pieces to obtain single-edge notched bend samples (SENB) conforming to the ISO 13586-1 standard test method for the determination of the plane-strain fracture toughness and strain energy release rate of plastic materials. Tests were performed by a 4052 Instron tensile testing machine at a cross-head speed of 1 mm/min. AFM and AFaM analyses were performed on the fracture surfaces of SENB specimens using an Nt-Mdt Solver P47H scanning probe microscope equipped with a piezoelectric sample holder. Nt-Mdt NSG silicon gold tips with nominally 5.5 N/m elastic constant and 150 kHz first resonance frequency were utilized. Calibrations were performed on an electronic grade (1 0 0) silicon wafer surface ($E = 130$ GPa, $\nu = 0.181$), previously cleaned from organic residues with chromic mixture and treated in HF (80% aq) for 30 min in an ultrasonic bath (Branson 2510, 47 kHz, 125 W) to remove the surface oxidized layer. Representative areas on the fracture surfaces of the composites and the unfilled matrix were selected to acquire topographic images (in contact and tapping mode) and amplitude-oscillation images (in tapping mode). Since all the samples were found to be homogeneous at a micrometric scale when observed