J. Phys. D: Appl. Phys. **33** (2000) 2347–2355. Printed in the UK PII: S0022-3727(00)09814-4

Heterodyne force microscopy of PMMA/rubber nanocomposites: nanomapping of viscoelastic response at ultrasonic frequencies

M T Cuberes†‡, H E Assender†, G A D Briggs† and O V Kolosov†

† Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
‡ Dpto. Mecánica Aplicada, Universidad de Castilla-La Mancha, Plaza Manuel de Meca 1, 13400 Almadén, Spain

Received 24 November 1999

Abstract. We present measurements of the nanoscale elastic and viscoelastic properties of samples of poly(methylmetacrylate) (PMMA)/rubber nanocomposites. For these studies we have used a new technique based on atomic force microscopy (AFM) with ultrasonic excitation, heterodyne force microscopy (HFM), which provides a means of testing the viscoelastic response of polymeric materials locally (in tip-probed regions) at MHz frequencies. Phase-HFM contrast distinguishes local differences in the dynamic response of PMMA/rubber composites. Comparison of HFM with other AFM-based techniques (ultrasonic force microscopy, friction force microscopy and force modulation microscopy), while imaging the same surface region, emphasizes the unique capabilities of HFM for these kinds of studies, and reveals key nanostructural characteristics of the composites. Some of the toughening particles appear to be broken down, with areas of PMMA detached from the surrounding matrix.

1. Polymer toughened polymers

Polymeric materials are able to show a very wide range of mechanical properties, determined by the orientation and the ease of motion of their component macromolecules. In some instances, the movement of molecular species involves co-operative motion over significant length scales. The viscoelastic nature of polymers means that their response to deformation may be highly dependent upon the time and length scales involved. It is usual for a multiplicity of relaxation processes to be available in response to a change in stress on the material. Where multiple phases and interfaces are present, for example as a result of blending polymers, and in polymer composites and thin film structures, the properties of the interfacial region are often critical to the performance of the material [1]. The mechanical behaviour of polymers at surfaces, interfaces or within nanometre-sized volumes is in general different to that of bulk macroscopic processes. The characterization of the nanoscale morphology and the dynamic mechanical response of interfaces and nanometre-scale volumes provide valuable insight to these issues [2].

The study presented here concerns a nanoscale polymer composite: a rubber toughened polymer acrylic copolymer material. The addition of rubber inclusions into thermoplastics is well-established for improving toughness. In a core-shell PMMA/rubber system, good adhesion between the acrylic matrix—a copolymer based upon poly(methylmethacrylate) (PMMA)—and the rubber is particularly important to achieve high performance. The toughening particles are composed of a core of acrylic enclosed with rubber with a bonded acrylic outer shell. This outer acrylic shell ensures good bonding to the matrix. Study of the nanoscale dynamic behaviour of these materials may help to understand the mechanisms that determine their ultimate impact resistance. The morphology at the surface of the sample is of particular interest as it is in this region where fracture will often initiate. Additionally, because of the rigours of an injection moulding process, the rubber inclusions (especially those close to the surface of the mould) may be distorted, elongated or damaged close to the mould surface where there are high stress and thermal gradients. Such distortions will play an important role in surface-initiated impact resistance.

Scanning force microscopy (SFM) techniques can, to certain extent, address the nanoscale viscoelastic behaviour as well as the nanoscale surface topography and other surface properties, such as adhesion. Such techniques have been applied to the study of polymeric materials. Topographic atomic force microscopy (AFM) images have already shown many morphological details of polymers: chain folding of molecules to form lamellae, spherulitic structures, fibres and different phases in polymer composites and blends, etc [3, 4]. Owing to its capability to probe tip–sample interaction forces, AFM also offers the possibility of investigating

0022-3727/00/192347+09$30.00