



Test method

Assessment of nanoparticle loading and dispersion in polymeric materials using oscillatory photon correlation spectroscopy



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ABSTRACT

The inclusion of small concentrations of nanoparticles in polymeric materials (≤ 5 wt. %) can significantly enhance material properties and functionality. However, poor or non-uniform particle dispersion resulting in particle clustering (agglomeration) in polymer nanocomposites (PNCs) limits the potential for property enhancement in these materials. Achieving good dispersion is considered essential for successful commercialization of PNCs. Hence, reliable and accurate measurement techniques for characterizing particle loading and dispersion would significantly contribute towards understanding and optimizing the material performance of PNCs, and consequently play a pivotal role in product development. This paper, the last of three papers on optical techniques, presents the results of a study using a dynamic light scattering technique, oscillatory photon correlation spectroscopy (Os-PCS), for discriminating between different particle loadings and levels of dispersion. The technique has been applied to two epoxy-based resin systems reinforced with either nanoclay platelets or silica microspheres.

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1. Introduction

The inclusion of small concentrations of nanoparticles (nanofillers) in polymers (≤ 5 wt. %) can potentially have a significant impact on material properties and functionality of the material. It is possible to improve material performance of polymeric nanocomposites (PNCs) to levels not achievable using larger (i.e. micron) size fillers in the same quantities [1–9]. The presence of nanoparticles can lead to significant enhancement in electrical and thermal properties, and to a lesser degree mechanical performance. Electrical and thermal conductivity have been observed to increase by a factor of 10^6 and 10^3 , respectively, by adding 1–2 wt. % of multi-walled carbon nanotubes (MWCNTs) [1,2]. Property enhancement is reliant on the nanoparticles being uniformly distributed throughout the polymer media. Dispersion of nanoparticles during mixing is, however, problematic, with inadequate mixing resulting in poor or non-uniform particle distribution and, consequently, particle agglomeration (or particle clustering), which subsequently limits the potential for property enhancement. Particle clustering can actually reduce mechanical properties, such as

fracture toughness. The general consensus is that a significant impediment to large-scale production and commercialization of PNCs is achieving good dispersion, and the absence of a reliable and accurate measurement technique capable of “quantitative” assessment of particle loading and dispersion suitable for production and in-service inspection is significantly delaying the development and application of PNCs.

A variety of techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), dielectrics and rheological characterization, ultrasonic resonance spectroscopy, scanning acoustic microscopy, laser-ultrasound, infrared spectroscopy, Raman spectroscopy and light transmission microscopy have been considered in an attempt to characterize particulate properties, such as size/shape (and distribution) and dispersion [3,8]. XRD is a versatile technique that can provide a wealth of information on the structural, physical and chemical nature of materials [5,10]. It is often used for characterizing the structure of PNCs, providing detailed information on the extent of intercalation (e.g. interlayer spacing d_{001}) and exfoliation of particulates. The positions and shapes of the peaks obtained from angular dependent intensity plots can provide information on the structure of the diffracting species and, in some cases, the degree of dispersion [5]. However, the results are difficult to interpret due to factors such as peak broadening resulting from the superposition of multiple peaks from incomplete intercalation, or complete loss of signal due to

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extremely poor dispersion [10]. TEM, a powerful although destructive technique, is capable of providing high-resolution images at the nanoscale. For TEM measurements, the samples need to be sufficiently thin (60–100 nm) to enable electron transmission. This poses particular problems in specimen preparation, requiring the use of an ultra-microtome. As the miniscule sample quantities (10^{-18} kg) involved are not representative of the bulk material, a large number of images are required in order to provide sufficient information on levels of loading and dispersion. Moreover, the structure of the material, and hence its physical properties, may alter as a result of the preparation process. Dielectric [11] and rheological [12] characterisation of polymeric melts can also indicate the level of particle loading and dispersion. Data interpretation tends to be difficult as different combinations of particle loading and dispersion can produce similar results. Ultrasonic resonance spectroscopy, scanning acoustic microscopy, laser-ultrasound, infrared spectroscopy, Raman spectroscopy and light transmission have been used with limited degrees of success for characterising nanoscale structures in PNCs, and again data interpretation is difficult [5,13–15].

The ability of the above-mentioned techniques to discriminate between different levels of particle loading and dispersion is extremely limited, especially for production and in-service inspection. The techniques often require special sample preparation (destructive in most cases), involve the analysis of extremely small sample areas and long measurement times, and quite often produce ambiguous results that are difficult to evaluate and interpret. Instrumentation and specimen preparation costs are often prohibitive, and require specialist knowledge of the techniques, thus rendering these techniques unsuitable for industrial usage, particularly in small and medium size enterprises. A more direct and rapid approach is required that provides accurate, repeatable “quantitative” measurements and is cost effective. It is worth noting that the degree of dispersion is generally described in qualitative terms (independent of the measurement technique employed), such as “good”, “moderate” or “poor”, rather than in quantitative terms – assessment tends to be highly subjective.

The National Physical Laboratory (NPL), UK, has investigated a number of non-invasive/non-destructive optical techniques utilising static and dynamic light scattering for determining loading and dispersion in semi- and fully-transparent polymeric solids to meet industrial requirements for production and in-service inspection of PNC materials and products. Static scattering techniques considered were frequency-domain optical coherence tomography (FD-OCT) [16–22] and optical wavefront correlation (OWC), previously designated as Fraunhofer wave correlation (FWC) [19,22,23]. The dynamic light scattering technique considered was oscillatory photon correlation spectroscopy (Os-PCS) [22,24]. Optical techniques can be used to examine PNCs as these materials often contain particulates with lengths in excess of a few microns (NB. According to the definition of a nanoparticulate, only a single dimension is required to be in nanometres). This coincides with wavelengths in the visible and near infrared spectrum. This paper, the last of three, focuses on the results obtained using Os-PCS, demonstrating that the technique is capable of discriminating between different levels of particle loading and dispersion in polymeric media for reasonably large sampling areas. The technique has been applied to two epoxy-based resin systems reinforced with either nanoclay platelets or silica microspheres. The results are compared with data obtained using FD-OCT and OWC (see also [20,23]).

2. Materials

Two epoxy-based PNC systems classified as Materials 1 and 2 (described below) have been investigated using Os-PCS.

2.1. Material 1

Silica microsphere reinforced epoxy, an Araldite[®] DBF epoxy resin with HY951 hardener (weight mix ratio of resin to hardener was 10:1), containing silica microspheres with an average diameter of 1.50 μm and loadings (0–1 wt. %) - see Table 1. The silica microspheres (suppliers Whitehouse Scientific) and epoxy resin were thoroughly mixed using a dual-centrifugal mixer SpeedMixer DAC150 PVZ/K, with typical spin cycles of 3500 rpm to minimise agglomeration of particles. The hardener was then added and centrifuge mixed. The mixed material was poured into small sample pots (~12 g) and then degassed for 3 min at a pressure less than 50 mbar to remove trapped air. Once degassed, the samples were placed in an oven at 60 °C and left for 48 h to ensure the epoxy resin was fully cured.

2.2. Material 2

Organoclay Nanomer[®] 1.30E, an octadecylamine modified montmorillonite, reinforced Huntsman LY 564 epoxy resin with Aradur 2954 hardener with varying particle loading (0–4 wt. %) and dispersion profiles (poor, moderate and good). The materials, listed in Table 2, were supplied by BAE Systems in the form of 3 mm thick autoclave cured plaques. The autoclave cure cycle consisted of an initial temperature ramp to 80 °C at 4 °C/min, dwell of 1 h at 80 °C followed by cooling to room temperature (15–18 h). Pressure was ramped to ~80 psi at 14 psi/min at the start of the cure cycle. The plaques were post-cured at 140 °C for 8 h. Average planar dimensions of the nanoclay particles (platelets) were $0.74 \pm 0.34 \mu\text{m}$ and $0.51 \pm 0.22 \mu\text{m}$, respectively. Intra-gallery (d_{001}) spacing is 1.8–2.2 nm (Nanocor technical datasheet for Nanomer[®] 1.30 E).

3. Experimental

3.1. Photon correlation spectroscopy (PCS)

Photon correlation spectroscopy (PCS), based on dynamic light scattering, is a well-established optical technique used to determine the size distribution profile and velocities of small (sub-micron to nanometre size) particles in liquids and gases [25–29]. A low power (10–40 mW) laser beam (high stability and coherent length) is scattered by particles suspended in a liquid or gas medium. The use of coherent light sources enables the formulation and use of the photocurrent auto-correlation function (ACF) for scattered light intensity [29] to enable a more accurate analysis of specific properties of small scattering volumes. Dispersed particles suspended in a liquid (or gas) medium undergo Brownian motion, causing fluctuations in the local concentration of the particles, resulting in local inhomogeneities of the refractive index and, subsequently, fluctuations in intensity of the scattered light. The Siegert relationship [30,31] yields the required ACF that enables the

Table 1
Density and weight fraction for the silica microsphere reinforced epoxy materials with different particle loadings.

Material	Density (g/cm^3)		Weight fraction (%) measured
	Measured	Predicted ^a	
Neat resin	1.1929 ± 0.0005	1.1929	0.000
0.1 wt. %	1.1941 ± 0.0007	1.1935	0.102
0.2 wt. %	1.1947 ± 0.0001	1.1941	0.200
0.5 wt. %	1.1959 ± 0.0005	1.1960	0.505
1.0 wt. %	1.1987 ± 0.0006	1.1989	0.994

^a Rule of mixtures calculations based on the measured weight fraction and density of silica microspheres ($1.8 \text{ g}/\text{cm}^3$), and measured density of the neat epoxy resin.

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