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Assessment of nanoparticle loading and dispersion in polymeric materials using optical wavefront correlation

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ABSTRACT

Small concentrations (≤ 5 wt. %) of nanoparticles in polymeric materials can potentially result in improvements in material properties and functionality. However, poor or non-uniform particle dispersion resulting in clustering (agglomeration) in polymer nanocomposites (PNCs) limits the potential for property enhancement. Achieving good dispersion is considered essential for large-scale production and commercialization of PNCs. New and effective measurement techniques capable of quantitatively 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 presents the results of a study using a static light scattering technique, optical wavefront correlation (OWC), for discriminating between different particle loadings and levels of dispersion. The technique has been applied to a range of PNCs, including epoxy resins reinforced with nanoclay platelets or silica microspheres, and zinc oxide and lithium aluminate reinforced polypropylene.

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1. Introduction

The inclusion of small concentrations of nanoparticles in polymers (≤ 5 wt. %) can have a significant impact on material properties (e.g. stiffness, strength, fracture toughness, thermal stability, fire retardancy, etc.) and functionality of polymer nanocomposites (PNCs), improving performance to levels not achievable using larger (i.e. micron) size fillers in the same quantities [1–7]. Property enhancement is reliant on the nanoparticles being uniformly distributed throughout the polymer media. Dispersion of nanoparticles during mixing is, however, problematic with poor mixing resulting in particle agglomeration (i.e. particle clustering) which, subsequently, limits the potential for property enhancement. 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 in-situ measurement technique for production and in-service inspection, capable of “quantitative” assessment of particle loading and dispersion, is significantly delaying the development and application of these materials.

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 distributions) and dispersion [1,6]. XRD is a versatile technique that can provide a wealth of information on the structural, physical and chemical nature of materials [3,8]. 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

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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 [3]. 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 extremely poor dispersion [8]. 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 [9] and rheological [10] 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 optical light transmission have been used with limited degrees of success for characterising nanoscale structures in PNCs, and again data interpretation is difficult [3,11–13].

The ability of the above-mentioned techniques to discriminate between different levels of loading and dispersion is very limited. 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 preparation costs are also often prohibitive and unsuitable for production or field inspection.

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 on-line and service inspection of PNC materials and products. Static scattering techniques considered were frequency-domain optical coherence tomography (FD-OCT) [14–18] and optical wavefront correlation (OWC), previously designated as Fraunhofer wave correlation (FWC) [19,20]. The dynamic light scattering technique considered was oscillatory photon correlation spectroscopy (Os-PCS) [19,20]. 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

nanoparticle only a single dimension is required to be in nanometres). This coincides with wavelengths in the visible and near infrared spectrum. This paper concentrates on the results obtained using OWC, 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 a range of PNCs including epoxy resins reinforced with nanoclay platelets or silica microspheres, and zinc oxide and lithium aluminate reinforced polypropylene.

2. Materials

Four different PNC systems classified as Materials 1–4 (listed below) have been investigated using OWC.

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 at levels of 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 then centrifuge mixed. The mixed material was poured into small sample pots (~12 g) and then degassed for 3 minutes 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 hours to ensure the epoxy resin was fully cured.

Material 2: Organoclay Nanomer® 1.30E, an octadecylamine modified montmorillonite, reinforced Huntsman LY 564 epoxy resin with Ardur 2954 hardener with varying particle loading (0 to 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 hour at 80 °C followed by cooling to room temperature (15–18 hours). 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 hrs. Average planar dimensions of the nanoclay particles (platelets) were 0.74 ± 0.34 mm and 0.51 ± 0.22 mm. Intra-gallery (d_{001}) spacing is 1.8–2.2 nm (Nanocor technical datasheet for Nanomer® 1.30 E).

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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