

Characterization techniques for nanotechnology applications in textiles

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Nanoscience and nanotechnology are considered to be the key technologies for the current century. Efforts are being made worldwide to create smart and intelligent textiles by incorporating various nanoparticles or creating nanostructured surfaces and nanofibres which lead to unprecedented level of textile performance, such as stain resistant, self-cleaning, antistatic, UV protective, etc. However, there are many challenges in the research and development of nanotechnology based products. The precise control of nanoparticle size, size distribution, dispersion at nanolevel and deposition on textile substrate needs sophisticated characterization techniques, such as particle size analyzer, electron microscopy (SEM/TEM/HRTEM), atomic force microscopy, X-ray diffraction, Raman spectroscopy, X-ray photon spectroscopy, etc. This paper discusses the basic principle and applications of these instrumental techniques in the field of nanotechnology research in textiles.

Keywords: Atomic force microscopy, Electron microscopy, Nanocomposite, Nanofibres, Nanomaterials, Particle size analyzer

1 Introduction

Over the past few decades nano size and nano dimensional materials whose structures exhibit significantly novel and improved physical, chemical and biological properties, phenomena, and functionality due to their nanoscaled size, have drawn much interest. Nanotechnology is an emerging interdisciplinary area that is expected to have wide ranging implications in all fields of science and technology such as material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, etc. Nanophasic and nanostructured materials are also attracting a great deal of attention of the textile and polymer researchers and industrialists because of their potential applications for achieving specific processes and properties, especially for functional and high performance textiles applications.

The nanotechnology research in the textile area mainly centres on creating unique properties in everyday fabric such as self-cleaning, water and oil repellency, stain proof, antibacterial, UV protective, antistatic, improved moisture regain and comfort in synthetic based textiles but without compromising the original hand, breathability and durability of the fabric. It also shows promising applications in developing advanced textile materials such as nanocomposite fibres, nanofibres and other

nanomaterial incorporated textiles for applications in medical, defence, aerospace and other technical textile applications such as filtration, protective clothing besides a range of smart and intelligent textiles.

The fundamental of nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range. But measuring this nano dimension is not a very easy task. Although research is going on to synthesise nanostructured and nanophasic materials, characterizing these nano sized materials is also an emerging field posing lot of challenges to scientists and technologists. Thus, nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano characterization techniques to allow a better control of morphology, size and dimensions of materials in nano range. The important characterization techniques used for nanotechnology research in textiles widely covering areas such as nanofinishing, nanocoating, nanocomposites and nanofibres have been reviewed in this paper.

2 Nanomaterial Characterization by Microscopy

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Further magnification cannot be achieved through optical microscopes due to aberrations and limit in wavelength of light. Hence, the imaging

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techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM/HRTEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. have been developed to observe the sub micron size materials. Though the principles of all the techniques are different but one common thing is that they produce a highly magnified image of the surface or the bulk of the sample. Nanomaterials can only be observed through these imaging techniques as human eye as well as optical microscope cannot be used to see dimensions at nano level. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

2.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (Fig. 1) is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves.¹

2.1.1 Basic Principle

When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back

scattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X-ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.

2.1.2 Applications

The SEM shows very detailed three dimensional images at much high magnifications (up to $\times 300000$) as compared to light microscope (up to $\times 10000$). But as the images are created without light waves, they are black and white. The surface structure of polymer nanocomposites, fracture surfaces, nanofibres, nanoparticles and nanocoating can be imaged through SEM with great clarity. As very high resolution images

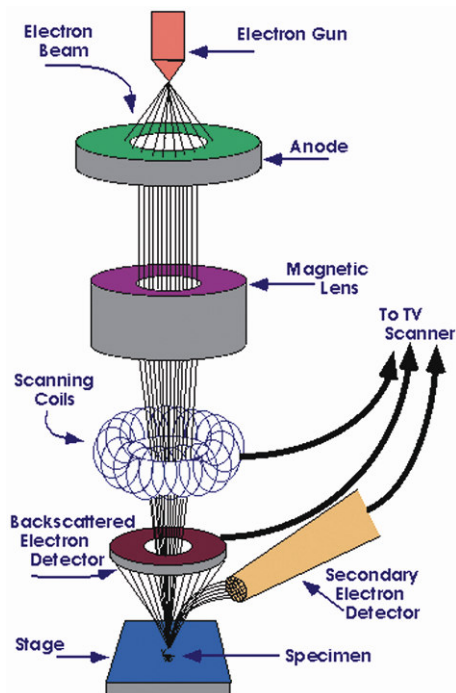


Fig. 1— Schematic diagram of SEM¹

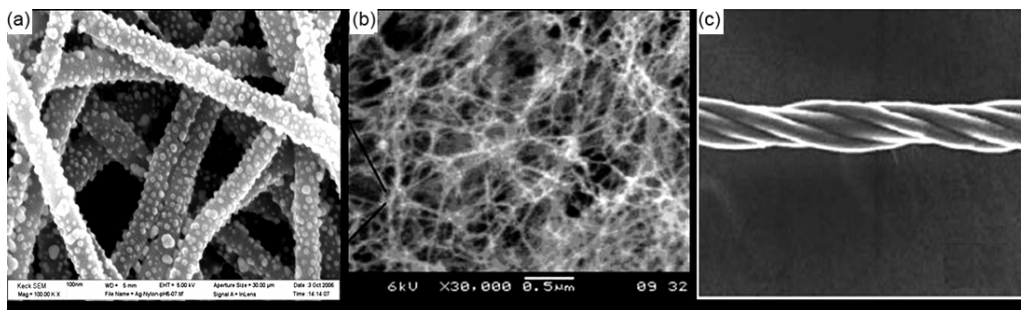


Fig. 2—(a) Electrospun nylon 6 nanofibres with surface bound silver nanoparticles², (b) peptide nanofibre scaffold for tissue engineering³, and (c) SEM image of plied CNT yarn⁴

of the dimension 1 – 5 nm can be obtained, SEM is the most suitable process to study the nanofibres and nano-coatings on polymeric/textile substrate.

Electrospun nanofibres are extensively studied in biomedical, environmental and other technical textile applications for their huge surface area. Electrospun nylon 6 nanofibres decorated with surface bound silver nanoparticles used for antibacterial air purifier can be characterized using SEM (Fig 2a).² In tissue engineering or cell culture applications, the SEM image is the prime characterization technique for scaffold construction, cell development and growth (Fig 2b).³ SEM technique (Fig. 2c) is used to observe the plied CNT yarns in 3D braided structures.⁴

The SEM technique can also be used to view dispersion of nanoparticles such as carbon nanotubes, nanoclays and hybrid POSS nanofillers in the bulk and on the surface of nanocomposite fibres and coatings on yarns and fabric samples (Fig. 3).^{5,6}

2.2 Energy Dispersive X-ray Analysis (EDX)

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample.

2.2.1 Basic Principle

This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not truly a surface science technique. By moving the electron beam across the material an image of each element in the sample can be obtained. Due to the low X-ray intensity, images usually take a number of hours to acquire.

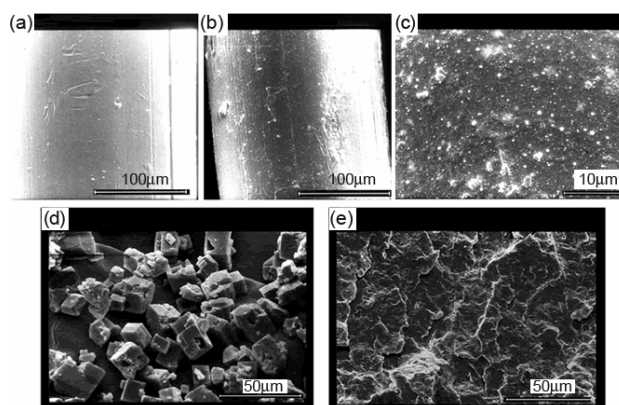


Fig. 3 —SEM surface images of (a) PP, (b & c) PP/clay nanocomposite filament, (d) POSS nanofillers, and (e) cross sectional view of HDPE/POSS nanocomposite fibre

2.2.2 Applications

The composition or the amount of nanoparticles near and at the surface can be estimated using the EDX, provided they contain some heavy metal ions. For example, the presence of Au, Pd and Ag nanoparticles on surface can easily be identified using EDX technique (Figs 4a-c). Elements of low atomic number are difficult to detect by EDX. The Si-Li detector protected by a beryllium window cannot detect elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) can be detected. EDX spectra have to be taken by focusing the beam at different regions of the same sample to verify spatially uniform composition of the bimetallic materials. Figure 4d shows how the incorporation of the silver nanoparticles in the cotton cloths can be verified by EDX.⁸

2.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen and interacts as passes

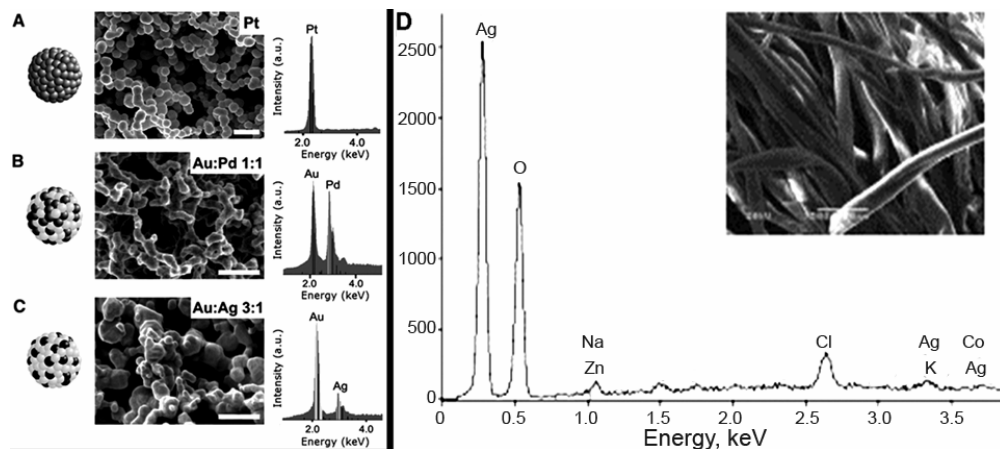


Fig. 4 —SEM images and EDX spectra of nanoporous materials made of (a) pure platinum, (b) 1:1 gold-palladium, (c) 3:1 gold-silver⁷ and (d) cotton cloth with silver nanoparticles⁸

through the sample. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen.

2.3.1 Basic Principle

The contrast in a TEM image is not like the contrast in a light microscope image. In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as ‘bright field’ or ‘light field’. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image.

The specimens must be prepared as a thin foil so that the electron beam can penetrate. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly produced by the deposition of a dilute sample containing the specimen onto support grids. As

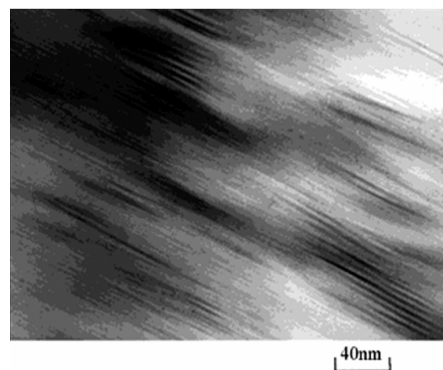


Fig. 5—TEM images of PP/MMT nanocomposites⁹

polymeric nanocomposites or the textile samples are not as hard as metals, they are cut into thin films (< 100 nm) using ultra-microtome with diamond knife at cryogenic condition (in liquid nitrogen).

2.3.2 Applications

The TEM is used widely both in material science/metallurgy and biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 micrometer. To withstand the instrument vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding.

The properties of nanocomposites depend to a large extent on successful nanolevel dispersion or intercalation/exfoliation of nanoclays, therefore monitoring their morphology and dispersion is very crucial. Figure 5 shows the TEM image of the PP/MMT nanocomposite with the clay content of

4.6 wt %. The dark line represents an individual clay layer, whereas the bright area represents the PP matrix.⁹ TEM images reveal the distribution and dispersion of nanoparticles in polymer matrices of nanocomposite fibres, nanocoatings, etc. The extent of exfoliation, intercalation and orientation of nanoparticles can also be visualized using the TEM micrograph.

2.4 High Resolution Transmission Electron Microscopy (HRTEM)

High resolution transmission electron microscopy is an imaging mode of the transmission electron microscope that allows the imaging of the crystallographic structure of a sample at an atomic scale.

2.4.1 Basic Principle

As opposed to conventional microscopy, HRTEM does not use absorption by the sample for image formation, but the contrast arises from the interference in the image plane of the electron wave with itself. Each imaging electron interacts independently with the sample. As a result of the interaction with the sample, the electron wave passes through the imaging system of the microscope where it undergoes further phase change and interferes as the image wave in the imaging plane. It is important to realize that the recorded image is not a direct representation of the samples crystallographic structure.

2.4.2 Applications

Because of its high resolution, it is an invaluable tool to study nanoscale properties of crystalline material. At present, the highest resolution possible is 0.8 Å. At these small scales, individual atoms and crystalline defects can be imaged. A typical HRTEM image of the material is shown in Fig.6 (ref. 10).

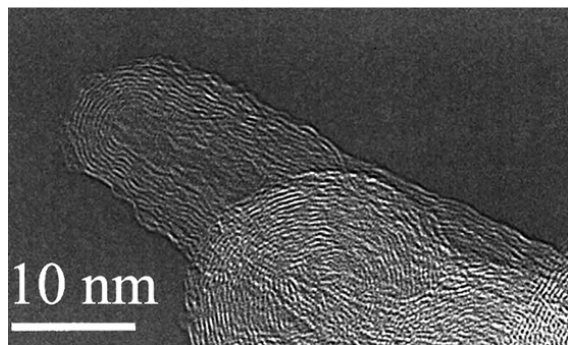


Fig. 6—HRTEM image of carbon onions¹⁰

2.5 Atomic Force Microscope (AFM)

The atomic force microscope (Fig. 7) is ideal for quantitatively measuring the nanometer scale surface roughness and for visualizing the surface nano-texture on many types of material surfaces including polymer nanocomposites and nanofinished or nanocoated textiles. Advantages of the AFM for such applications are derived from the fact that the AFM is non-destructive technique and it has a very high three dimensional spatial resolution.

2.5.1 Basic Principle

The basic principle and applications of atomic force microscopy have been the subject of a number of excellent reviews.¹²⁻¹⁴ In atomic force microscopy, a probe consisting of a sharp tip (nominal tip radius is in the order of 10 nm) located near the end of a cantilever beam is raster scanned across the surface of a specimen using piezoelectric scanners. Changes in the tip specimen interaction are often monitored using an optical lever detection system, in which a laser is reflected off of the cantilever and onto a position-sensitive photodiode. During scanning, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. There are three scan modes for AFM, namely contact mode, non contact mode and tapping mode.

In contact mode, the tip scans the specimen in close contact with the surface of the material. The repulsive force on the tip is set by pushing the cantilever against

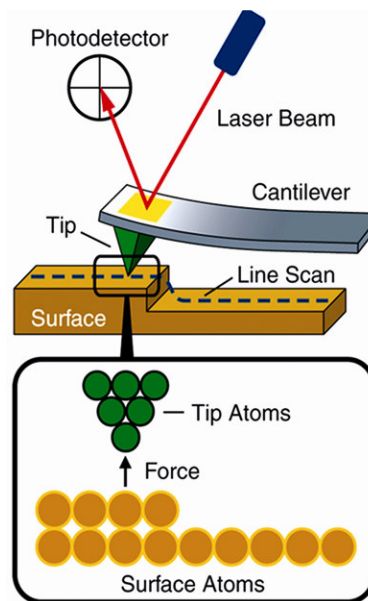


Fig. 7—Schematic diagram of AFM¹¹

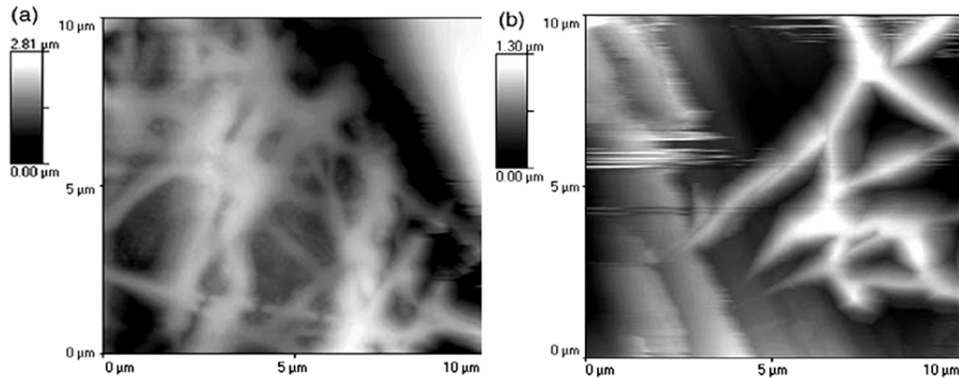


Fig. 8—AFM images of (a) nanofibres and (b) nanofibres laid on nonwoven substrate

the specimen's surface with a piezoelectric positioning element. The deflection of the cantilever is measured and the AFM images are created. In non-contact mode, the scanning tip hovers about 50–150 Å above the specimen's surface. The attractive forces acting between the tip and the specimen are measured, and topographic images are constructed by scanning the tip above the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at its resonant frequency (often hundreds of kilohertz) using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate when the tip is not in contact with the surface of a material. The oscillating tip is then moved towards the surface until it begins to tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000–500,000 cycles/s. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to measure the surface characteristics.

2.5.2 Applications

The use of this new tool is of importance in fundamental and practical research and development of versatile technical textiles for a variety of applications. Atomic force microscopy can be used to explore the nanostructures, properties, and surfaces and interfaces of fibres and fabrics. For example, structural characteristics of nanofibre materials, nanolevel surface modification of textile surfaces (by plasma or UV eximer lamp, etc) can be easily assessed by this sophisticated technique. AFM provides powerful tools for nondestructive characterization of textiles. The image in Fig. 8a (ref. 15) shows the three-dimensional fibrous web,

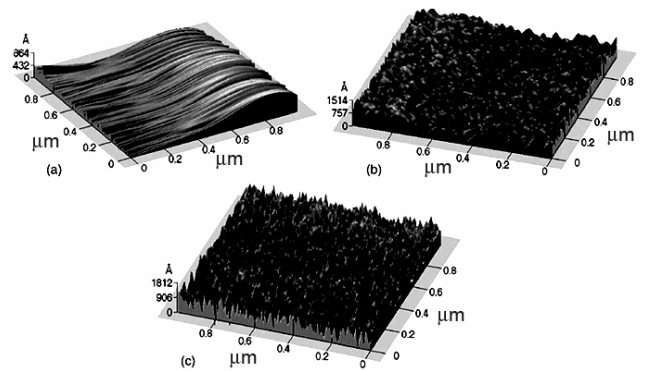


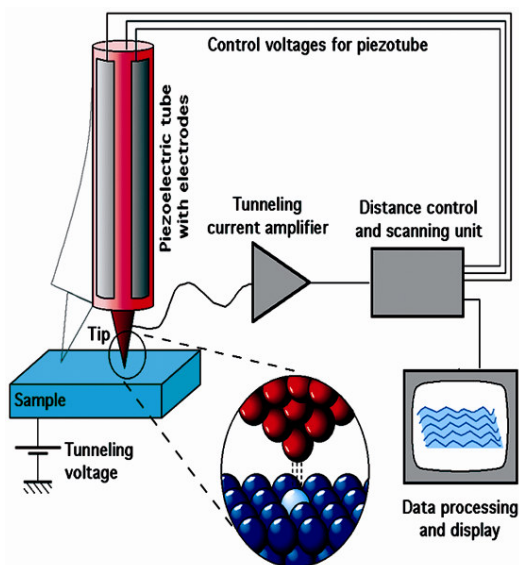
Fig. 9—3D views of non-contact mode AFM images of PET textile surface (Scan area 1 μm × 1 μm) (a) untreated surface, (b) 60s plasma treated surface, and (c) 120s plasma treated surface

consisting of fibres with diameters ranging from <300 nm to > 1000 nm. The fibres are randomly oriented and the pores with varying sizes are formed. The image also indicates that the diameter is uneven along an individual fibre. Figure 8b (ref. 15) is an AFM image showing the nanofibres laid onto an ordinary nonwoven substrate.

A possible way to investigate the effect of plasma processing on the morphology of the textile surfaces is given by AFM. AFM images of the untreated and air plasma treated PET textile, after an exposure time to the air plasma of 60 s and 120 s, are shown in Fig. 9 (ref. 16). Changes in the morphology of surface modified textile samples can also be quantified by root-mean-square (rms) surface roughness and surface area values.¹⁶

2.6 Scanning Tunneling Microscopy (STM)

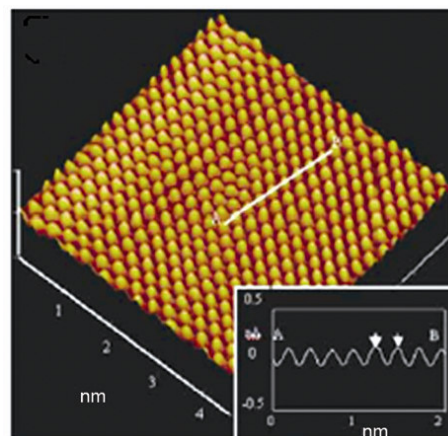
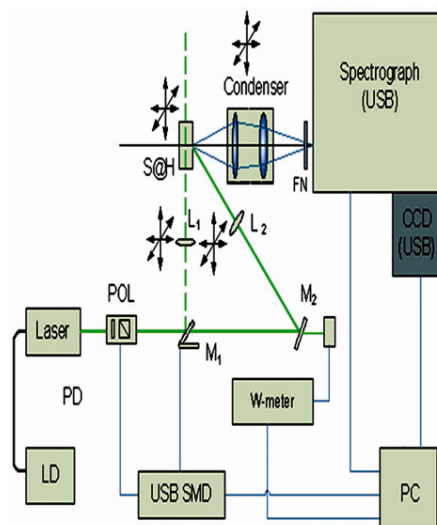
Scanning tunneling microscopy (Fig. 10) is an instrument for producing surface images with atomic-scale lateral resolution, in which a fine probe tip is scanned over the surface of a conducting specimen, with the help of a piezoelectric crystal at a distance of

Fig. 10— Schematic view of an STM¹⁷

0.5–1 nm, and the resulting tunneling current or the position of the tip required to maintain a constant tunneling current is monitored.

2.6.1 Basic Principle

The principle of STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to a metallic or semi-conducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them. For low voltages, this tunneling current is a function of the local density of states at the Fermi level of the sample. Variations in current as the probe passes over the surface are translated into an image. For STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. They normally generate images by holding the current between the tip of the electrode and the specimen at some constant value by using a piezoelectric crystal to adjust the distance between the tip and the specimen surface, while the tip is piezoelectrically scanned in a raster pattern over the region of specimen surface being imaged by holding the force, rather than the electric current, between tip and specimen at a set-point value. Atomic force microscopes similarly allow the exploration of nonconducting specimens. In either case, when the height of the tip is plotted as a function of its lateral position over the specimen, an image that looks very much like the surface topography results. The STM can be used not only in ultra high vacuum but also in air and various other liquid or gas, at ambient and wide range of temperatures. STM can be a

Fig. 11—Highly oriented pyrolytic graphite sheet under STM¹⁹Fig. 12—Schematic diagram of Raman spectrometer²¹

challenging technique, as it requires extremely clean surfaces and sharp tips.

2.6.2 Applications

Scanning tunneling microscopy is a powerful tool in nanotechnology and nanoscience providing facilities for characterization and modification of a variety of materials. STM is successfully used to detect and characterize materials like carbon nanotubes (single-walled and multi-walled) and graphene layer (Fig. 11) (ref. 18). The instrument has also been used to move single nanotubes or metal atoms and molecules on smooth surfaces with high precision.^{19, 20}

3 Nanomaterials Characterization by Spectroscopy

3.1 Raman Spectroscopy

Raman spectroscopy (Fig.12) is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other

low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic laser light. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system.

3.1.1 Basic Principle

The Raman effect occurs when light impinges upon a molecule, interacts with the electron cloud of the bonds of that molecule and incident photon excites one of the electrons into a virtual state. For the spontaneous Raman effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, which generates Stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-Stokes Raman scattering. A molecular polarizability change or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

3.1.2 Applications

Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It therefore provides a fingerprint by which the molecule can be identified in the range of 500-2000 cm^{-1} . Raman gas analyzers have many practical applications. For instance, they are used in medicine for real-time monitoring of anaesthetic and respiratory gas mixtures during surgery. In solid state physics, spontaneous Raman spectroscopy is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal.²²

Raman active fibres, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibres also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes. Study on polycarbonate/MWCNT composite shows Raman shift (Fig. 13) under strain for both AR-MWCNT (as received MWCNT) and EP-MWCNT (surface epoxy

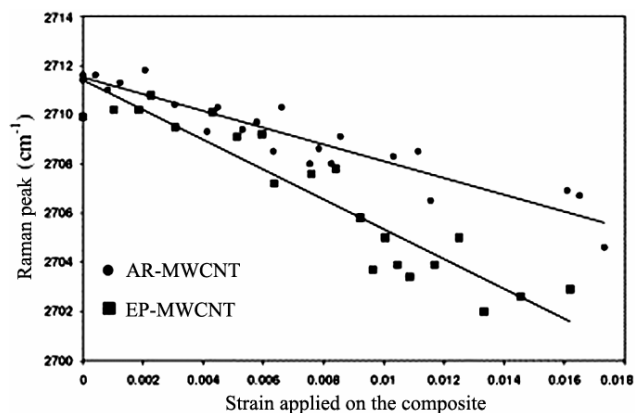


Fig. 13—Shift in the Raman peak as a function of applied strain²³

modified MWCNT) as carbon nanotube (CNT) is a Raman active material.²³

3.2 Ultraviolet-Visible (UV-VIS) Spectroscopy

Ultraviolet spectrophotometers consist of a light source, reference and sample beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as a Xenon lamp.

3.2.1 Basic Principle

The reference beam in the spectrophotometer travels from the light source to the detector without interacting with the sample. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. When the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital, energy is absorbed. The detector records the ratio between reference and sample beam intensities (I_0/I). The computer determines at what wavelength the sample absorbed a large amount of ultraviolet light by scanning for the largest gap between the two beams. When a large gap between intensities is found, where the sample beam intensity is significantly weaker than the reference beam, the computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum.²⁴

3.2.2 Applications

In certain metals, such as silver and gold, the plasmon resonance is responsible for their unique and remarkable optical phenomena. Metallic (silver or gold) nanoparticles, typically 40–100 nm in diameter, scatter optical light elastically with remarkable efficiency because of a collective resonance of the

conduction electrons in the metal known as surface plasmon resonance. The surface plasmon resonance peak in UV absorption spectra is shown by these plasmon resonant nanoparticles. The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance associated with a nanoparticle are dependent on the particle's size, shape, and material composition, as well as the local environment.

Besides biological labelling and nanoscale biosensing silver nanoparticles have received considerable attention to the textile and polymer researchers due to their attractive antimicrobial properties. The surface plasmon resonance peak in absorption spectra of silver particles is shown by an absorption maximum at 420-500 nm. The surface peaks vary with size, shape and concentration of the metallic nanoparticles. Figure 14 (ref. 25) shows how the value of λ_{\max} is shifted towards higher wavelengths with increasing Ag content ($\lambda_{\max} = 398$ nm at 5×10^{-4} M Ag sol and $\lambda_{\max} = 406$ nm at 5% Ag/kaolinite) in a silver nanoparticle/kaolinite composites. It is reported²⁶ that the truncated triangular silver nanoparticles with a [111] lattice plane as the basal plane displayed the strongest biocidal actin compared with spherical, rod shaped nanoparticles or with Ag⁺ (in the form of AgNO₃). This shape of the silver nanoparticles can be identified by observing the corresponding peak.

Figure 15 (ref. 27) shows the spectrum of an individual red, green, and blue particle, and the high-

resolution TEM images of the corresponding particle are shown above their respective spectrum. This example is a representative of the principle conclusion that the peak shifts as per the particle shape and the triangular shaped particles appear mostly red, particles that form a pentagon appear green, and the blue particles are spherical.

The optical absorption spectra of metal nanoparticles shift to longer wavelengths with

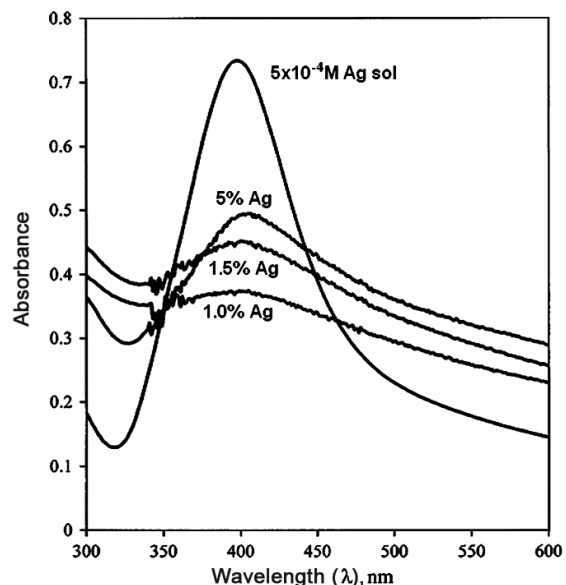


Fig. 14—UV- Vis absorption spectrum of 5×10^{-4} M Ag sol and spectra of suspensions of Ag/kaolinite samples at different silver contents (1, 1.5 and 5% Ag)

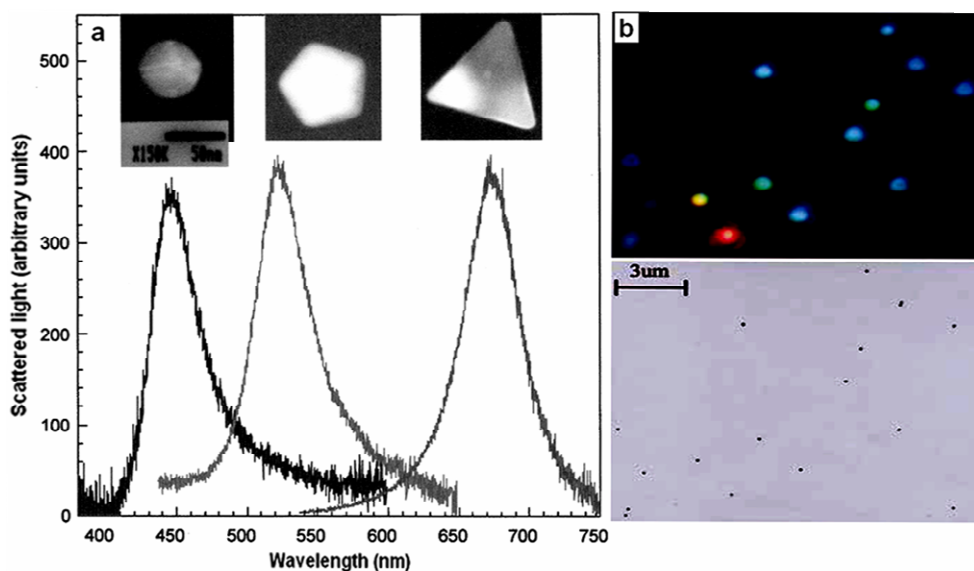


Fig. 15— (a) Optical spectroscopy measurements of individual silver nanoparticles of different shapes and (b) colour image of a typical sample of silver nanoparticles as viewed under the dark field microscope (top picture), and a bright field TEM image of the same collection of silver nanoparticles (bottom picture)²⁷

increasing particle size.²⁸ The position and shape of the plasmon absorption of silver nanoclusters are strongly dependent on the particle size, dielectric medium, and surface-adsorbed species.²⁹ According to Mie's theory³⁰ only a single surface plasmon resonance (SPR) band is expected in the absorption spectra of spherical nanoparticles, whereas anisotropic particles could give rise to two or more SPR bands depending on the shape of the particles. The number of SPR peaks increases as the symmetry of the nanoparticle decreases.³⁰ Thus, spherical nanoparticles, circular disks, and triangular nanoplates of silver show one, two and more peaks respectively.

Figure 16 (ref. 31) shows some typical UV–VIS spectra of the suspension after the reactants had been mixed and sonicated under an atmosphere of air for different periods of time at 27°C. In this case, the colour of the solution started to change from colourless to light brown after the reaction had proceeded for 15 min. This change in colour suggests the formation of silver nanoparticles in the solution.

4 Characterization of Nanomaterials by X-ray

4.1 Wide Angle X-Ray Diffraction

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.

4.1.1 Basic Principle

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with

scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg's law or equation.³² As each crystalline material including the semi crystalline polymers as well as metal and metal oxide nanoparticles and layered silicate nanoclays have a characteristic atomic structure, it will diffract X-rays in a unique characteristic diffraction order or pattern.

4.1.2 Applications

X-ray diffraction data from polymers generally provide information about crystallinity, crystallite size, orientation of the crystallites and phase composition in semi crystalline polymers. With appropriate accessories, X-ray diffraction instrumentation can be used to study the phase change as a function of stress or temperature, to determine lattice strain, to measure the crystalline modulus, and with the aid of molecular modelling to determine the structure of polymer.

Besides the above-mentioned characterization this sophisticated technique can also be used to characterize polymer-layered silicate (clay) nanocomposites. Polymer/layered silicate nanoclay composites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties at very low clay content (3–6 wt %), when compared with virgin polymer or conventional composites. The use of organoclays as precursors to nanocomposite formation has been extended into various polymer systems (thermoset and thermoplastic) including epoxy and others.

For true nanocomposites, the clay nanolayers must be uniformly dispersed and exfoliated in the polymer

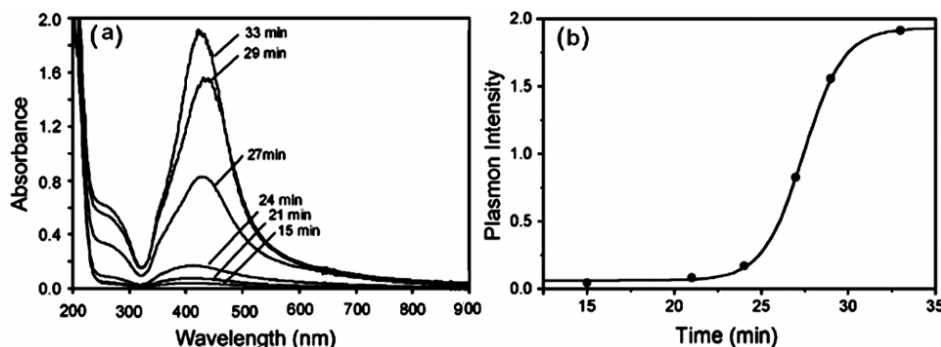


Fig. 16—(a) UV–Vis absorption spectra taken from a reaction solution after the reactants had been mixed and sonicated in air at 27 °C for different periods, and (b) a plot of the intensity of the plasmon peak vs reaction time

matrix. The structure of polymer/layered silicates composites has typically been established using wide angle X-ray diffraction (WAXD) analysis. By monitoring the position, shape and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height.³³

Organophilic clay (also known as nanoclay) can be obtained by simply the ion-exchange reaction of hydrophilic clay with an organic cation such as an alkyl ammonium or phosphonium ion to make it compatible with polymeric matrix. The inorganic ions, relatively small (sodium), are exchanged with more voluminous organic *onium* cations.³⁴ This ion-exchange reaction results in widening the gap between the single sheets, enabling organic cations chain to move in between them. This increase in *d*-space or degree of exfoliation of the polymer nanocomposite can be obtained from Bragg equation. The X-ray diffractograms³⁵ of the organoclay reveals a shift in the position of [001] planes (2θ changed from 5.7° to 4.32°), indicating an increase in the basal spacing of these planes (Fig. 17). The increase is relatively large from 1.5 nm to 2.06 nm and confirms the occurrence of organic molecule intercalation between silicate platelets.

4.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (Fig. 18) is a quantitative spectroscopic surface chemical analysis technique used to estimate the empirical formula or elemental composition, chemical state and electronic state of the elements on the surface (up to 10 nm) of a material. XPS is also known as ESCA, an abbreviation of electron spectroscopy of chemical analysis.

4.2.1 Basic Principle

X-ray irradiation of a material under ultra-high vacuum (UHV) leads to the emission of electrons from the core orbitals of the top 10 nm of the surface elements of the material being analyzed. Measurement of the kinetic energy (KE) and the number of electrons escaping from the surface of the

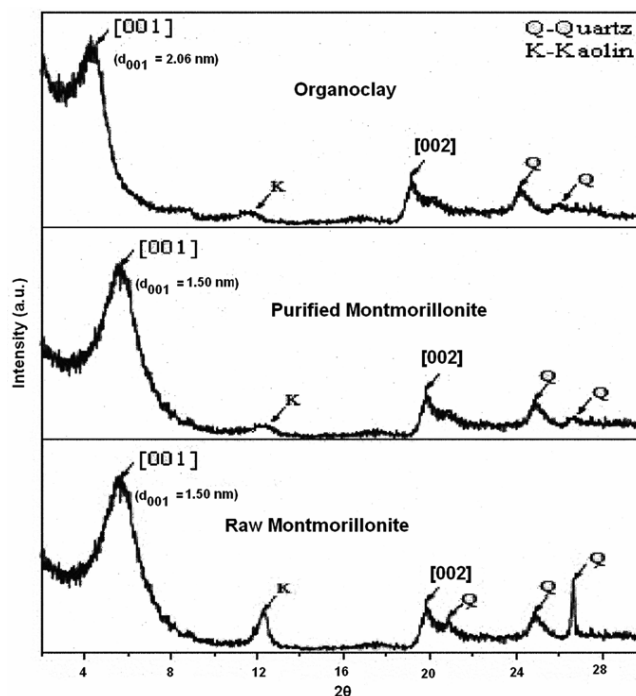


Fig. 17—WAXD patterns for raw montmorillonite (MMT), purified montmorillonite and organoclay

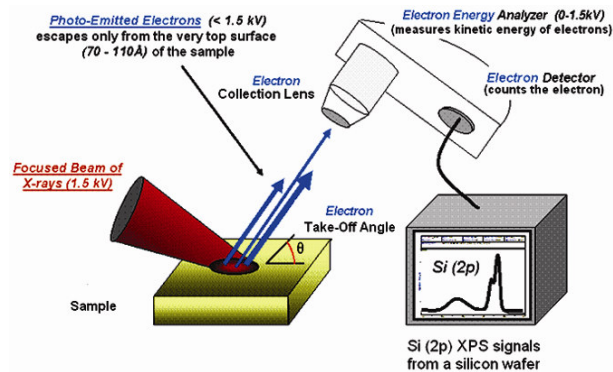


Fig. 18—Schematic view of XPS³⁶

material gives the XPS spectra. From the kinetic energy, the binding energy of the electrons to the surface atoms can be calculated. The binding energy of the electrons reflects the oxidation state of the specific surface elements. The number of electrons reflects the proportion of the specific elements on the surface.

As the energy of a particular X-ray wavelength used to excite the electron from a core orbital is a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using the following equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi$$

where E_{binding} is the energy of the electron emitted from one electron configuration within the atom; E_{photon} , the energy of the X-ray photons being used; E_{kinetic} , the kinetic energy of the emitted electron as measured by the instrument; and Φ , the work function of the spectrometer (not the material).³⁷

4.2.2 Applications

XPS is used to determine the elements and the quantity of those elements that are present within ~10 nm of the sample surface. It also detects the contamination, if any, exists in the surface or the bulk of the sample. If the material is free of excessive surface contamination, XPS can generate empirical formula of the sample and the chemical state of one or more of the elements can be identified. Moreover, the technique can be used to determine the thickness of one or more thin layers (1–8 nm) of different materials within the top 10 nm of the surface. It can also measure the uniformity of elemental composition of textile surfaces after nanolevel etching, finishing or coating of the surfaces. The only limitation is that it cannot detect hydrogen ($Z=1$) or helium ($Z=2$), because these two elements do not have any core electron orbitals, but only valence orbitals.

Figure 19 (ref. 38) is an example of a wide scan survey spectrum using XPS which can be used to determine the elements present and not present on a modified and unmodified textile surface. Figure 20a (ref. 39) illustrates a survey spectrum of an

unmodified sample of woven cationic cotton. As expected, distinctive peaks at 281.91 and 528.91 eV indicate the presence of carbon and oxygen respectively. A trace amount of N (nitrogen), generated during the cationization process, was also detected at 398.91 eV. Figure 20b (ref. 43) shows a survey spectrum of a 20-layer PSS/PAH polyelectrolyte film supported on a woven cationic cotton substrate. The distinctive peaks at 398.91 eV and 164.91 eV have been previously used by several research groups to monitor the presence of N and S originated from the PAH and PSS layers respectively.

5 Particle Size Analyzer

There are different techniques for the measurement of particle size and its distribution (PSD) such as sieve analysis, optical counting methods, electro resistance counting methods, sedimentation techniques, laser diffraction methods, dynamic light scattering method, acoustic spectroscopy, etc. Among them dynamic light scattering is mostly used for obtaining size

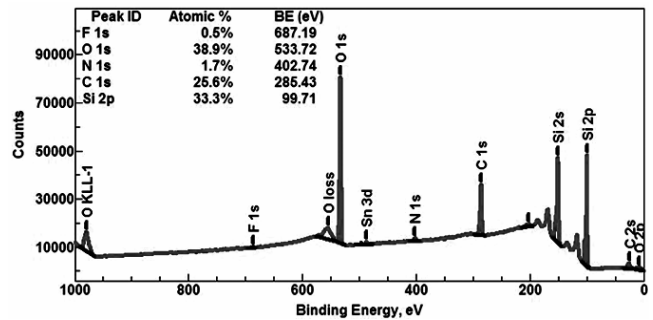


Fig. 19—Wide XPS scan survey spectrum for all elements

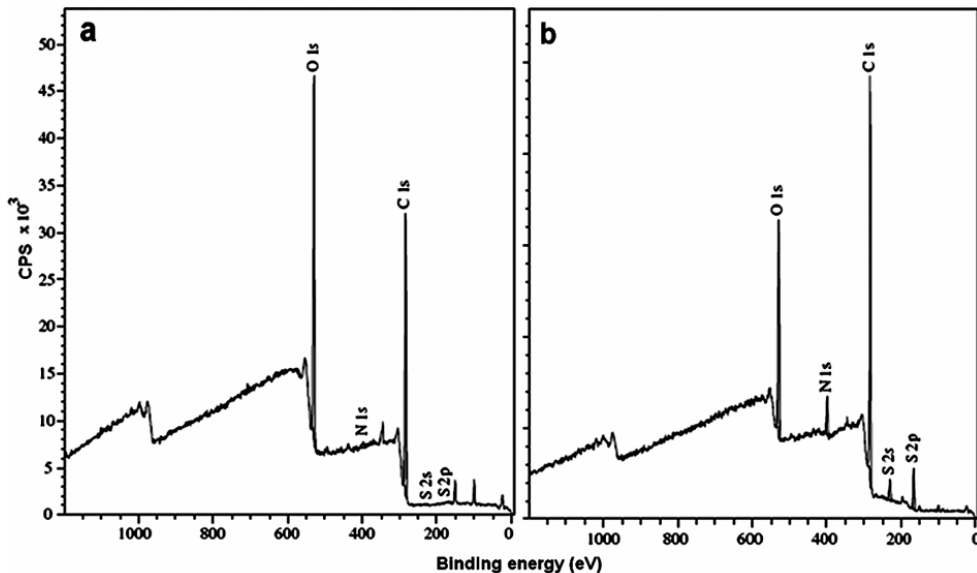


Fig. 20—XPS spectra for (a) cationically charged woven cotton fabric and (b) cationically charged woven cotton fabric supporting 20 self-assembled layers of PSS/PAH

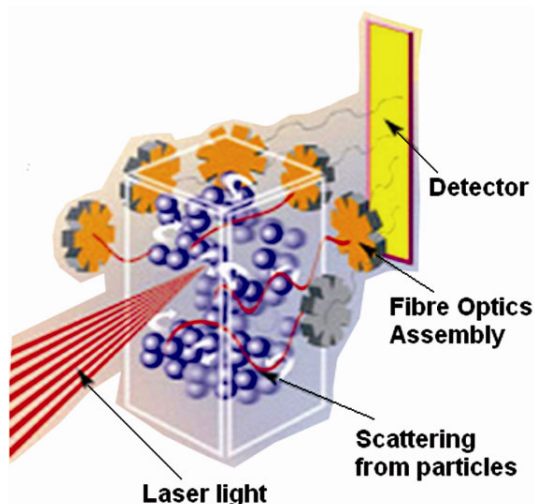


Fig. 21—Schematic diagram of particle size analyzer⁴⁰

distribution of nanoparticles.

5.1 Basic Principle of Dynamic Light Scattering (DLS)

Dynamic light scattering, sometimes referred to as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS) (Fig. 21) is a non-invasive, well-established technique for measuring the size of molecules and particles typically in the submicron region, and with the latest technology lower than 1 nanometre.

Particles, emulsions and molecules in suspension undergo Brownian motion. This is the motion induced by the bombardment of solvent molecules that themselves are moving due to their thermal energy. If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are “kicked” further by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size (radius r_k) using the Stokes-Einstein relationship⁴¹, as shown below:

$$r_k = \frac{kT}{6\pi\eta D}$$

where k is the Boltzmann's constant; T , the temperature in K; η , the solvent viscosity; and D , the diffusion coefficient.

5.2 Applications

Silver, titanium, silica and zinc oxide nanoparticle are often used in textile substrates to get improved functionality of the nanoparticle finished textile materials. For example, TiO₂ nanoparticles size and

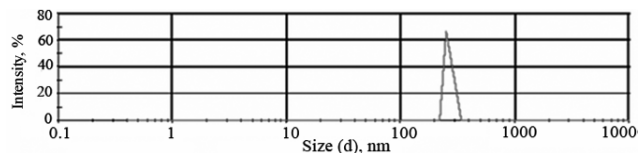


Fig. 22—Size distribution of TiO₂ nanoparticles using DLS

size distribution (Fig. 22) can be studied using DLS technique.⁴² The enhanced property is dependant on the size of the applied nanoparticles, which generally have a tendency to agglomerate. Therefore, size and size distribution study of the nanoparticle in the dispersion as well as suspension is important before applying to the textile substrates.

6 Conclusions

The current trend of R & D activities in advanced materials, polymers and textiles clearly indicates a shift to nanomaterials as the new tool to improve properties and gain newer multi functionalities. However, challenges and the success for the researchers in this emerging field would depend to a large extent on the availability, cost and ease of handling and performance of the sophisticated instrumental techniques described in this paper. Further, the quality and extent of information derived through these techniques i.e. SEM, TEM, AFM and Raman spectroscopy, also depends to a large extent on the level of understanding of the user, expertise and right sample preparation. As far as textile materials such as fibres, yarns, finished and coated fabrics are concerned, the dispersion, impregnation or immobilization of nanoparticles on textile surfaces can be studied through appropriate use of these techniques. However, handling of textile samples poses a lot of challenges and limitations due to their flexible, uneven and non uniform surfaces. For TEM/HRTEM, the sectioning of ultra-thin wafers from resin embedded fibre, yarn or fabric on a cryo ultra-microtome requires skill and patience of the user. Thus, it can be summarised that nanotechnology research in textiles has a lot of potential as a futuristic approach but would be largely governed by simultaneous progress in the newer, faster, simpler and more efficient characterization techniques for nanomaterials, nanocoatings and nanocomposites used in textile applications.

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