Characterization of Silver/Polymer Nanocomposites

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Abstract In this chapter, we mainly discussed the characterization techniques of polymer nanocomposites based on silver nanoparticles. The main characterization techniques discussed in this chapter includes various methods such as microscopic and spectroscopic characterizations, scattering and diffraction characterizations, thermal, mechanical and viscoelastic characterizations of polymer/silver nanocomposites. The commonly used instruments through which the analysis of morphology, microstructure, elemental composition, mechanical, thermal and viscoelastic properties of silver/polymer composites are discussed in this chapter. The following is a detailed description of each characterization techniques.

1 Microscopic Analysis on Silver/Polymer Nanocomposites

To determine the size and distribution of the Ag hybridized polymer, scanning electron microscopy (SEM) analysis can be used. SEM is a kind of microscopic morphology observation method with size range between transmission electron microscopy (TEM) and optical microscopy (OM). It can be directly used to the sample surface for microscopic imaging. Secondary electron signal imaging is mainly used to observe the surface morphology of the sample, i.e. scanning the sample with a very narrow electron beam, which produces various effects through the interaction between the electron beam and the sample, mainly the secondary electron emission of the sample. Secondary electrons can produce an enlarged image of the sample's surface, which is set up in time sequence when the sample is scanned; even if the enlarged image is obtained by point-by-point imaging. It is a large instrument for measuring the surface morphology of samples. When an

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incident electron beam with certain energy bombards the surface of the sample, the electrons collide with the nucleus and outer electrons of the element in one or more elastic and inelastic collisions. Some electrons are reflected out of the surface of the sample, while the other electrons infiltrate into the sample, gradually lose their kinetic energy, and finally stop moving and are absorbed by the sample. In this process, more than 99% of the incident electron energy is converted to the thermal energy of the sample, while about 1% of the incident electron energy excites various signals from the sample. These signals mainly include secondary electrons, backscattered electrons, absorption electrons, transmission electrons, Auger electrons, electromotive force, cathode-luminescence, X-ray and so on. Thus, SEM is to obtain the observation of the surface morphology of the test sample by receiving, amplifying and displaying the information, and then analyze the samples.

To observe the surface morphology by SEM, the sample preparation process is simple and does not need to be sliced. The samples should be treated accordingly to keep the surface structure of the samples as good as possible, without distortion and pollution, and the samples should be dry and have good conductivity. SEM also can observe the surface structure of samples directly. Since the sample moves and rotates in a three-dimensional space in the sample chamber, the sample can be observed from various angles. Moreover, it has stereoscopic sense, wide amplification range, high resolution and little damage and pollution to the sample. SEM analyses the morphological and structural characteristics of the material by the signals collected from the collision between the electron beam and the sample surface. For the observation of the morphology and structure of silver nanoparticles based polymer nanocomposites, because of the high resolution and clear image of scanning electron microscopy, the profile characteristics, cross-sectional area view, thickness and distribution of silver nanocomposite material can be judged and analyzed by scanning electron microscopy.

Moreover, it can be used for analysis of various functions. When it is connected with X-ray spectrometer, the morphology can be observed and the composition of micro-area can be analyzed at the same time. When equipped with optical microscope and monochrometer, the cathode fluorescence image can be observed and the cathode fluorescence spectrum can be analyzed. The dynamic test can be carried out on a heating, cooling and stretching test bench. Understanding the most basic form of a substance begins with its morphology, and further in-depth analysis of its elemental composition and the micro-structure of its formation. SEM is usually used in conjunction with X-Ray fluorescence (XRF) thickness measurement and EDX. Some EDX machines also have XRF thickness measurement functions. From the relevant common analysis reports, we can see both the SEM diagram of the sample and the result chart of the analysis and measurement.

The advantages and advancement of nanoparticles are due to their nanoscale size. The unique properties of nanoparticles cannot be separated from their ultrafine size. Therefore, the research on the size of silver polymer nanocomposites are the premise and foundation for the good application of these nanocomposites. SEM images could verify the existence of silver nanoparticles, in which form they exist and whether they form dense network structures or are completely embedded below the surface of polymers. At the same time, the existence of large black spots or not would help to judge whether the silver nanoparticle polymer was aggregated or not from the image. SEM images can be used to judge whether silver nanoparticles are uniformly distributed in the matrix of the polymer as well as the influence of polymer introduction on the dispersion of silver nanoparticles (Fig. 1).

For example, when graphene oxide was introduced in the silver/graphene oxide hydrogel, the silver nanoparticles were well dispersed on the surface of graphene suggested by SEM (Jiao et al. 2015). In this case, the introduction of polymer played a good role in the dispersion of silver nanoparticles. As it is well known, porous structure is the basic structure of polymer, which has many advantages, such as large contact area, strong adsorption capacity and so on. SEM can clearly characterize the porous structure of silver nanocomposites and as the content of silver nanoparticles variation. The radius of silver nanoparticles obtained by using low concentration silver ion solution is smaller than that using high concentration silver ion solution. The radius of silver nanoparticles obtained by using high concentration silver ion solution is larger. For example, in graphene oxide hydrogels, the most basic structure is porous structure. Different silver content has a great influence on the size of the hole, which lead to the decrease of the effectiveness of

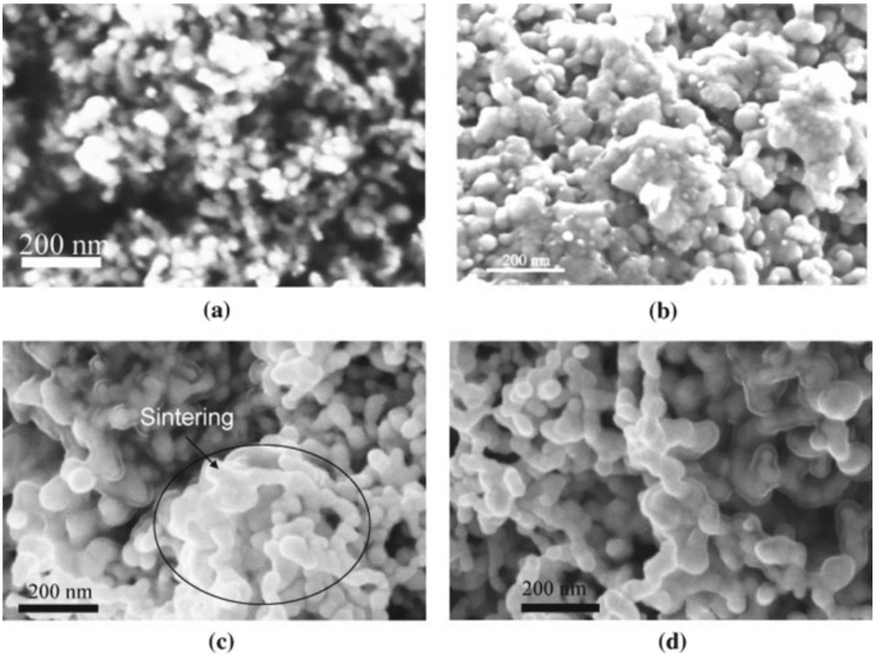


Fig. 1 Morphology difference of silver nanoparticles before annealing with the mixture of bisphenol A and hexahydro-4-methylphthalic anhydride (HMPA) **a** non-annealed, **b** annealed at 150°C for 30 min, **c** annealed at 100°C for 30 min, and **d** annealed at 100°C for 30 min. Reproduced from Ref. Jiang et al. (2006) with permission

hydrogel. With the increase of silver content, the larger the pore structure and radius are, the larger the surface area is, which is conducive to the adsorption of other substances. So the radius has a great influence on the properties of polymers. Scanning electron microscopy (SEM) can be used to analyze the radius of silver nanoparticles with different content, which can create better polymer structure (Fan et al. 2014). Furthermore, the contact structure between silver nanoparticles can be analyzed simultaneously.

Since SEM can observe the micro-structure of polymer very well, thus, tiny changes of the micro-structure of silver/polymer interface could be monitored through SEM (Fig. 2). In this way, the formation mechanism of silver/polymer nanocomposites through comparing the changes of the micro-structure before and after the formation of composites could be understood. In the preparation of silver nanowire-based transparent electrodes, when the initial intense pulsed light (IPL) irradiation intensity is very low, it is obvious that silver nanoparticles are randomly distributed on the polymer surface. The edges of these silver nano-networks are very sharp and not fully fused with the polymer, but there are gaps at the junction of the silver nanoparticles with the polymer. When the irradiation intensity increases, the polymer begins to melt. The melted polymer filled the gap, and the silver nanoparticles begin to embed beneath the surface of the polymer. The parts far away from the polymer are still very clear. When the irradiation intensity increased, the degree of melting increased until it is completely embedded below the surface, forming a perfect physical viscous form with the polymer. The cross section and the formation process of silver/polymer composite were observed by SEM. The surface structure of the composite and the micro-structure between silver nanoparticles were analyzed, indicating potential application for the implementation of this electrode (Song et al. 2015). To further observe morphology in higher magnification, TEM is mainly used to analyze the fine structure (less than 200 nm) that cannot be seen clearly under an optical microscope and SEM. These structures are called submicroscopic structures or ultra-fine structures. If people want to see these structures clearly, a shorter wavelength electron beam as the light source is necessary. The wavelength of the electron beam is much shorter than that of visible light and ultraviolet light. The current resolution of TEM can reach 0.2 nm. Because the penetrating power of electron beams is very weak, the specimens used for electron microscopy must be made into ultra-thin sections with a thickness of about 50 nm. It plays a very important role in the research and application of new materials. It has a wide range of applications in materials science such as the analysis of organic-inorganic composite materials and to study the composition, microstructure and dispersion of composite materials.

In contrast, optical microscope (abbreviated as OM) is an optical instrument that uses optical principles to magnify and image tiny objects that cannot be distinguished by the human eye, so that people can extract detailed structure information. Ordinary optical microscopes cannot see 1 nm which has to be observed under TEM. The microscope uses the magnification imaging principle of the convex lens to magnify the small objects that the human eye cannot distinguish to the size that

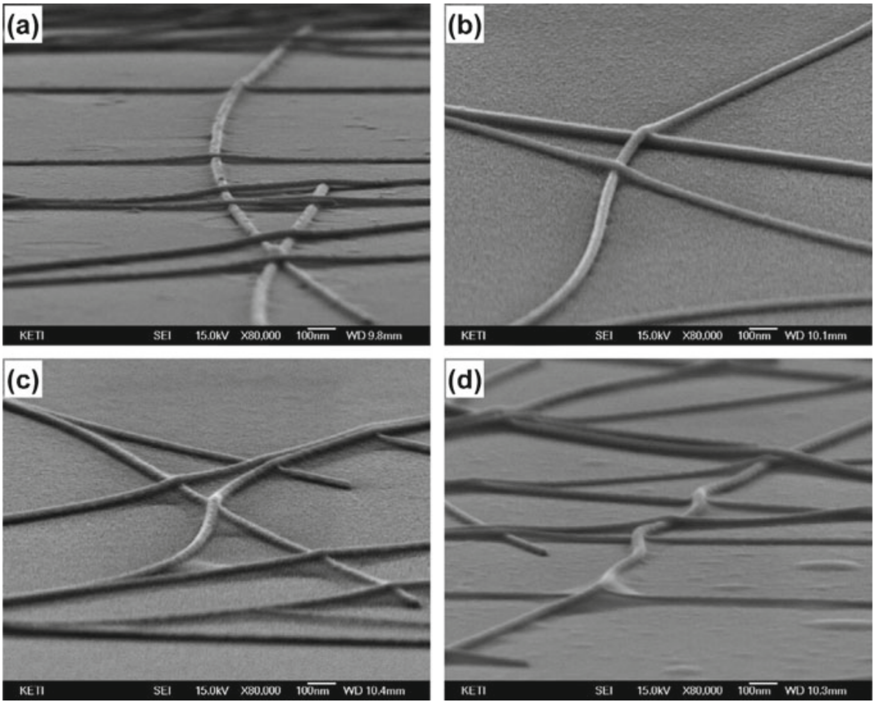


Fig. 2 Tilt-views taken by SEM for samples with increasing number of IPL exposure (500 ls): **a** a single exposure, **b** 2 times, **c** 4 times, and **d** 8 times. Reproduced from Ref. Song et al. (2015) with permission

the human eye can distinguish. It mainly increases the opening angle of the close small objects to the eye (The object with a large angle of view has a large image on the retina.), use the angular magnification M to represent their magnification power. The maximum magnification would be thousands of times. The detailed description on application of TEM and OM on characterization of Ag NPs have been discussed on Chapter 4 and hence they are not discussed here.

2 Spectroscopic Analysis of Silver/Polymer Nanocomposites Analysis

2.1 Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive X-ray spectrometer (EDX) is realized by analyzing the characteristic X-ray wavelength and intensity of the elements emitted by the samples. The elements in the samples are determined according to the different characteristic

X-ray wavelengths of different elements. The content of elements in the sample can be determined by comparing the strength of the specific lines of different elements. Usually EDX combined with electron microscopy can be used to analyze the micro-area components of samples.

The whole atomic system is in an unstable excited state due to the appearance of holes by the inner electron. The atomic lifetime of the excited state is about 10^{-12}–10^{-14} s, and then it spontaneously transits from high energy state to low energy state. This process is called relaxation process. The relaxation process can be either non-radiative or radiative. When the outermost electrons transit to holes, the energy released is absorbed inside the atom and driven out of another outermost secondary photoelectron, which is called Auger effect, also known as secondary photoelectron effect or non-radiation effect. The ejected secondary photoelectron is called Auger electron. The energy is characteristic and independent of the energy of incident radiation. When the energy released by the outer electrons leaps into the inner hole and it is not absorbed by the atom, X-ray fluorescence is produced in the form of radiation. The released energy is equal to the energy difference between two energy levels. Therefore, the energy or wavelength of X-ray fluorescence is characteristic and shows one-to-one relationship with elements. When the K-layer electrons are ejected, the holes can be filled by any electron in the outer layer, which can produce a series of spectral lines called K-line. The X-ray from L-layer to K-layer is called K-alpha ray, and the X-ray from M-layer to K-layer is called K-beta ray.

In addition, the intensity of fluorescence X-ray has a certain relationship with the content of the corresponding elements. Therefore, the quantitative analysis of elements can be carried out.

EDX can characterize the local chemical composition of inhomogeneous samples, the chemical composition of less materials or small particles, the one-dimensional or two-dimensional component distribution of inhomogeneous samples, and the film composition deposited on arbitrary substrates. Qualitative analysis of elements in samples and quantitative analysis of their mass concentration can be carried out quickly. Solids can be directly analyzed, and it is a non-destructive characterization technology, requiring little or no sample preparation, and the sample preparation process is simple. To obtain reliable analysis results, the samples are required to be: (1) the samples are strict, smooth and smooth (especially for quantitative analysis, the samples need polishing), and the atomic number less than five cannot be analyzed. (2) Samples with rough surface can be analyzed, but they are limited to qualitative and semi-quantitative analysis, and the existing forms of elements cannot be analyzed. (3) The sample must be conductive and conductive, and the surface should be sprayed with carbon or gold if necessary.

Typical EDX spectra: the y-axis describes the number of X-rays, and the x-axis is the energy of X-rays. The data generated by EDX analysis contains the spectra corresponding to the peaks of all the different elements in the sample. The location of the peak is to identify the elements, and the peak height is helpful to quantify the concentration of each element in the sample. Characteristic of energy spectrum: it can quantitatively analyze all elements in various types of micro-area, and it can be completed very quickly in a few minutes. The geometric position of sample and detector is low, the requirement of W and D is not very strict, and the results of X-ray scanning and surface distribution can be obtained at low magnification; the probe current of energy spectrum analysis is small, and the damage to the sample is small; the detection limit is generally 0.1–0.5%, medium. The quantitative phase error of the main elements of the non-overlapping peaks of atomic number is about 2%.

Qualitative elemental analysis of silver/polymer composite can be done by EDX spectroscopy. The characteristic X-rays emitted by different elements have different frequencies, i.e. different energies. Elements can be determined by detecting the energies of different photons. The data generated by EDX analysis contains the spectra corresponding to the peaks of all the different elements in the sample. Each element has a characteristic peak of unique energy. By analyzing the energy of the characteristic peak, the elements contained in the polymer composite could be inferred. For example, in the analysis of silver nanoparticles polymer, we can qualitatively judge the appearance of silver nanoparticles in polymer by observing the appearance of characteristic peaks of silver. Different elements have different characteristics. Quantitative elemental analysis of silver/polymer composite also can be done by EDX spectroscopy. Quantitative analysis of EDX energy spectrum can be divided into two methods. One is quantitative analysis with standard sample. Under the same conditions, the X-ray intensity of each element is identified in the standard sample and the composite sample is measured simultaneously. The percentage of each element can be calculated by strength ratio. Therefore, the accuracy of standard sample analysis is high. The second is quantitative analysis method is without standard sample. X-ray intensity of the sample is calculated quantitatively by theoretical calculation or database. In silver/polymer nanocomposites, EDX can be used to determine the percentage of each element in the polymer. Not only the existence of silver nanoparticles and other particles are expected to be characterized, but also the content of each particle. EDX can be combined with other spectrograms to analyze the content of each element, so as to obtain the proportion of each kind of element. In cellulose/silver polymer composite, different characteristic peaks in EDX represent carbon, oxygen, and iron, silver and gold. The ratio of each element is characterized by the simultaneous use of Mapsum spectrum beside it (Maleki et al. 2017). When silver nanoparticle is doped into polymer matrix, its performance is affected not only by the way in which the composite is formed, but also by the specific elements that make up the polymers. Therefore, through the quantitative analysis, the effect of element content on the properties of polymer could be understood in detail. The properties of polymer can be modulated by changing the content of elements in polymer, and the application of silver/polymer nanocomposite in various fields can be expanded.

EDX can be combined with electron-probe micro-analyzer (EPMA), SEM, TEM and so on. The combination of SEM and EDX is the most widely used microanalysis instrument. SEM equipped with EPMA accessories such as X-ray energy spectrum IEDX and X-ray component analysis can analyze the chemical composition and other information in the sample micro-area.

The lower limit of the detected component content is 0.1%. It also can be used to analyze the modification of dry polymer materials. EDX can not only detect the presence of silver nanoparticles in the analysis of silver nanocomposites, but also judge the dispersion of silver nanoparticles in the polymer matrix. Through the EDX images, if silver nanoparticles are not aggregated, they will be uniformly distributed on the polymer surface. It is proved that silver nanoparticles are well dispersed on the surface at least. In cellulose/silver polymer composite, SEM was combined with EDX to characterize the dispersion of silver nanoparticles (Fig. 3). The results showed that silver nanoparticles were uniformly distributed on the surface of polymer, which proves that silver nanoparticles are well dispersed in the polymer matrix. Each instrument has its own defects. When several instruments are used to analyze polymers together, they can better characterize the polymers (Maleki et al. 2017).

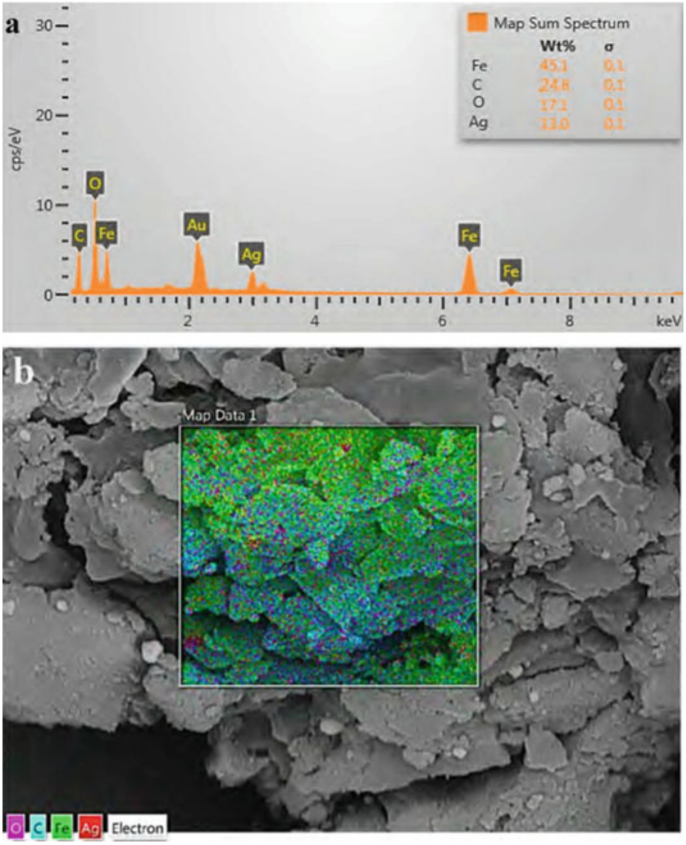


Fig. 3 **a** EDX analysis of the magnetic cellulose. **b** SEM-EDX mapping. Reproduced from Ref. Maleki et al. (2017) with permission

2.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis uses X-ray to irradiate the sample and excite the inner electrons or valence electrons of atoms or molecules. The electrons stimulated by photons are called photoelectrons. The photoelectron spectra can be obtained by taking the kinetic energy of photoelectrons as abscissa and the relative intensity (pulse/s) as ordinate.

XPS is widely used in the analysis of inorganic compounds, alloys, semiconductors, polymers, elements, catalysts, glass, ceramics, dyes, paper, ink, wood, cosmetics, teeth, bones, transplants, biological materials, grease, glue and so on. The composition of typical XPS spectra includes abscissa: electron binding energy or kinetic energy, which directly reflects the shell/level structure of electrons, and ordinate: CPS (counts per second): relative photoelectron current intensity, the peak directly represents the binding energy of atomic orbits and the background is bremsstrahlung (primary and secondary electron generation of inelastic scattering). The number of back electrons with high binding energy increases gradually. Many peaks can be obtained by scanning the sample. The strongest photoelectron line in the main line is usually the peak with the strongest intensity, the smallest peak width and the best symmetry in the spectrum. It is called the main line in XPS spectrum. The photoelectron line is used to identify elements. In addition to strong photoelectron lines, there are photoelectron lines from other shell layers in the atom, but the intensity is slightly weak, some are very weak. The spectral line width of the photoelectron line is a contribution from four aspects: the natural width of the intrinsic signal of the sample element, the natural width of the X-ray source, the instrument and the broadening factor of the sample's own condition. There are other accompanying peaks or lines in the spectra, such as multiple splitting lines, which help to analyze the spectra and provide important information for the study of electronic structures in atoms.

XPS can be used in:

1. Qualitative analysis of elements. All elements except H and He can be identified according to the position of the characteristic lines in the energy spectrum.
2. Quantitative analysis of elements. The atomic content or relative concentration is determined by the intensity of the photoelectron spectrum line (the area of the photoelectron peak) in the energy spectrum.
3. Solid surface analysis. It includes chemical composition or element composition of surface, valence state of atom, energy state distribution of surface, electron cloud distribution and level structure of surface electrons.
4. Structure of compounds. The chemical shift of the inner electron binding energy can be measured accurately, and the information of chemical bond and charge distribution can be provided.
5. The application of molecular biology. i.e. A small amount of CO in vitamin B_{12} could be identified by XPS.

In the characterization of silver/polymer nanocomposite by XPS, the elements in silver nanocomposites can be qualitatively analyzed. According to the different chemical energy and frequency of each element, the intensity of the characteristic main line formed in the spectrum is different, and the particles in silver nanocomposite can be inferred. It can also be used to characterize the change of the intensity of the characteristic main line when the content of silver nanoparticles changes. It can not only analyze the elements existing in silver nanocomposites, but also analyze the chemical structure and energy level structure of the elements. It can specifically characterize the existing form of silver nanoparticles. It can further characterize the properties of the polymer, and has great significance in improving the material and their application. The specific analysis of silver/polymer nanocomposite is as follows.

XPS spectra prove the existence of polymer and determine the form of elements in silver nanocomposite and the corresponding chemical bond type of elements. Each element (except H and He) has its own strongest photoelectron line with characterization, which is the main basis for qualitative analysis of elements. XPS spectrogram characterizes the signal of each element in silver nanocomposites at specific bond energy. Different polymers are composed of different chemical elements, and each element has its own unique crystal structure. Then there are differences in the characteristic peaks in the corresponding spectrogram. Several characteristic main lines appear, which represent several elements. So we can deduce what elements exist in the polymer and what types of bonding elements are by mapping the different bond energies of each element. In the silver/polydopamine composite, the XPS spectrum (Fig. 4) includes several characteristic lines, which is assigned to carbon, nitrogen, oxygen and silver particles, respectively. There are three bond types in the C1s map, carbon-carbon single bond or C–Hx (284.1 eV), carbon-nitrogen bond or C–OH (285.2 eV), carbon-oxygen double bond (287.9 eV), from the N1s map, nitrogen-hydrogen bond can be obtained at bond energy 399.4 eV. O1s map mainly contains two kinds of signals, carbon-oxygen double bond (530.4 eV) and oxygen-hydrogen bond (532.1 eV). The existence of polydopamine can be inferred from these results. The signal of silver nanoparticles can be also obtained, which appears at about 370 eV (Zhang et al. 2015). Therefore, by observing several different characteristic lines and different bond energies in the spectra, we can infer the existence of elements in polymers and the different bonding forms of different elements.

XPS can not only qualitatively determine the presence of elements in polymer, but also quantitatively analyze silver nanocomposites. Quantitative analysis of different chemical structures can be carried out according to the area of different peaks. The relationship between the characteristic peaks and the content of silver nanoparticles can be obtained by XPS in-depth analysis in silver/polymer nanocomposite. The characteristic main line strength of each element will be affected by other elements, where the intensity of the peak of the element will change. When silver nanoparticles are incorporated into the polymer, the peak strength of elements in the polymer will change. When the content of silver nanoparticles is higher, the effect of silver nanoparticles on the characteristic

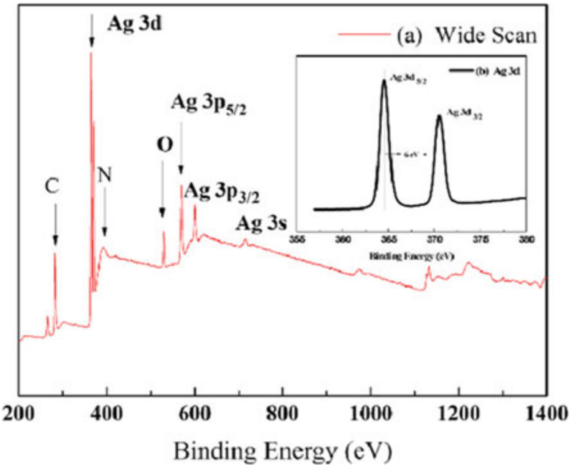


Fig. 4 XPS spectra of AgNPs@PDA particles (Zhang et al. 2015). Reproduced from Ref. Zhang et al. (2015) with permission

mainline strength of other elements is greater. For example, when the mass ratio of silver nanoparticles in graphene oxide changes, the characteristic of silver nanoparticles in XPS spectra will be different. With the increasing content of silver nanoparticles, the characteristic main line strength of C1s decreases gradually. The influence of the content of silver nanoparticles on the XPS spectra and the influence of the content of silver nanoparticles on the main line strength of carbon elements are also explained. It shows that the presence of adjacent elements affects the structural characteristics of polymers to certain extent (Fan et al. 2014).

In addition to the main line, there are also many splitting lines in XPS spectra. The reason is that when the valence shell of atoms has unpaired spin electrons (e.g. transition elements in D region, lanthanide elements in F region, most gas atoms and a few molecules NO, O_2, etc.), the inner vacancies formed by photoionization will couple with them, resulting in more than one final state of the system, which is reflected in the splitting of spectra in XPS spectra. In XPS spectra, the splitting lines of spin-orbit coupling energy levels are usually obvious. The main splitting lines are: $p_{3/2}$, $p_{1/2}$ of p orbital, $d_{3/2}$, $d_{5/2}$ of d orbital and $f_{5/2}$, $f_{7/2}$ of f orbital. The energy splitting distance varies with the element. However, not all elements have obvious spin-orbit coupling splitting spectra, and the energy spacing of splitting varies with chemical states. When silver nanoparticles exist, the internal chemical structures are different, and the energy levels are different in the polymer. The characteristic peaks under different bond energies represent different orbital forms in silver nanoparticles. Therefore, energy level and charge distribution information of silver nanoparticles in silver/polymer composites can be easily analyzed according to the characteristic peaks of XPS. In the XPS spectra of a silver/polydopamine (Fig. 4), the spectra of silver nanoparticles can be observed. There are two different peaks in the spectra, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ at 368.1 eV and 374.1 eV bond energies respectively, which proves that the energy level structure of silver nanoparticles is different (Zhang et al. 2015).

2.3 Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy

Ultraviolet-visible (UV-vis) absorption spectra belong to molecular spectra. They are all produced by the transition of valence electrons. In organic compounds, there are σ electrons forming single bonds, π electrons forming double bonds, and n-pair electrons without bonds. When a molecule absorbs a certain amount of radiation energy, these electrons will jump to a higher energy level. At this time, the orbit occupied by the electrons is called anti-bond orbit, which is closely related to the internal structure. In the UV-vis spectra, there are four types of electron transitions: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The energy required for various transition type decreases in the following order: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$. Accordingly, the composition, content and structure of substances can be analyzed, determined and inferred.

Detection can be qualitatively and quantitatively when the matter undergoes n-π^* and π-π^* transition upon light irradiation.

Lambert-Beer's law is the theoretical basis of quantitative analysis in UV-vis spectroscopy. It is mathematical expressed as $A = \varepsilon\ b\ c$. where ε is the molar absorptivity (sometimes called the extinction coefficient), c is the concentration of the solution in moles per liter, and l is the length in centimeters of the sample through which the light passes.

UV-vis spectroscopy is widely used, not only for quantitative analysis. UV-vis spectroscopy also has been particularly useful in identifying the impurities in polymers such as monomer inhibitors residuals and simple structural analysis, equilibrium constants, coordination ratios of complexes, etc. because of its sensitivity ($\sim 10^{-5}$ molar).

UV-vis spectra of substances are basically chromophores (referring to the atomic groups or structural systems that can absorb ultraviolet and visible light) absorption in their molecules. Conjugated systems do absorb there, however, and the greater the conjugation, the longer the wavelength of maximum absorption. UV-vis spectra can be chosen for the understanding of the chromophore information of silver/polymer nanocomposites. Because of its high sensitivity, the UV-vis peaks of silver nanoparticles are usually only two or three, and the peak shape is gentle. It mainly depends on the chromophore characteristics, which conforms to Bill's law, so it is suitable for qualitative and quantitative study of silver nanoparticles. The silver nanoparticle polymers are characterized from several aspects.

According to Lambert-Bill's law, same concentration of solution measured has different absorbance at different wavelengths of light. The absorbance of the same substance at different concentrations is different at a certain wavelength, especially the maximum absorption wavelength. For the same solution to be measured, the higher the concentration, the greater the absorbance will be. For the same substance, regardless of the concentration, the wavelength corresponding to the maximum absorption peaks the same, and the shape of the curve is exactly the same. In the characterization of silver/polymer nanocomposite, the concentration of solution can be changed to change the content of silver nanoparticles. Through the characterization of ultraviolet-visible absorption light, the change of absorption peak intensity can be observed from the obtained curves. Therefore, the change of silver nanoparticles on the peak intensity can be analyzed. Because it is the same substance, its absorption wavelength has no effect. By observing the absorption peak height at the same wavelength, the influence of solution concentration on polymer can be deduced.

UV-vis spectroscopy can be used to analyze the existence of silver nanoparticles. For example, by comparing the absorption peaks in the ultraviolet-visible absorption spectra of silver nanoparticles with those of non-silver nanoparticles, we can judge whether silver nanoparticles are incorporated into polymers. If silver nanoparticles are not existed polymers, no absorption peaks will be observed (Chen et al. 2015).

Ultraviolet-visible absorption spectra can characterize the state of silver nanoparticles in polymers. The absorption peak is due to the plasma resonance of nanoparticles, which is related to the size and shape of nanoparticles. When there are nanoparticles, it will appear absorption peaks, which can identify the existence of silver nanoparticles. For example, in the silver/graphene oxide hydrogel, the plasma resonance of silver colloidal results in the appearance of absorption peaks, which indicates that silver, exists as nanoparticles in the silver graphene oxide complex (Fan et al. 2014). When silver nanoparticles are assembled into polymer matrix, the characteristic peak absorption wavelength of UV-vis spectrum changes, which may be due to the reduction of the distance between adjacent silver nanoparticles in the film compared with silver nanoparticles in aqueous solution (Fig. 5), indicating that the size and morphology of silver nanoparticles can change when they interacted with polymers (Chen et al. 2015).

Each polymer has different chemical bonds. The types of chemical bonds also can be analyzed by UV-vis spectroscopy. UV-vis spectroscopy can be used to

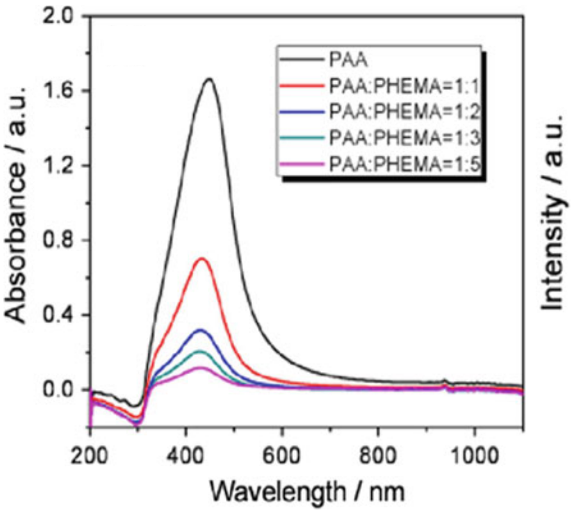


Fig. 5 UV-Vis spectra of different polymer films contained Ag NPs, where PAA stands for polyacrylic acid, PHEMA stands for poly (2-hydroxyethyl methacrylate). The Ag was generated by soaking the coated PAA:PHEMA film in a 0.3 M aqueous solution of $AgNO_3$ for 12 h before UV irradiation. Reproduced from Ref. Chen et al. (2015) with permission

deduce whether there are conjugated structure systems in the molecular skeleton of compounds, such as C=C–C=C, C=C=O, benzene ring, etc. We can judge how electrons transit. Different conjugated systems correspond to different absorption peaks at different wavelengths. By analyzing several absorption peaks, we can judge how many conjugated systems there are and how many transitions there are. By comparing the types of chemical bonds, the formation process and the formation mechanism can be analyzed. UV-vis spectra show two absorption peaks in silver/graphene oxide hydrogel composites which is 232 and 300 nm, representing the π-π* transition of carbon-carbon double bond electrons and the n-π* transition of carbon-oxygen double bond electrons (Fan et al. 2014).

The formation of new chemical bonds can be judged by UV-vis spectra. When silver nanoparticles react with polymers, new chemical bonds, such as hydrogen bonds and covalent bonds, are formed. This is important to the formation of polymer composites. Through the characterization of silver nanoparticles polymer by UV-vis spectroscopy, the changes of absorption peaks before and after polymer reaction can be used to judge the formation of some new chemical bonds, and also prove the formation of polymers. For example, in the silver nanowire/chitosan composite films, silver enhanced the properties of polymers by forming silver-sulfur covalent bonds. Therefore, the formation of covalent bonds is the key to the formation of polymers. UV-vis absorption spectra were used to analyze nanowire/chitosan composites and silver nanowire mixed chitosan polymers respectively. By comparing the absorption peaks formed by the polymers before and after the analysis, the change of absorption peak intensity can be observed obviously. The formation of silver-sulfur covalent bond is proved (Pan et al. 2018).

2.4 Infrared Spectroscopy (IR)

Infrared Spectrum (IR) is also called molecular vibration rotation Spectrum. It is caused by the transition of molecular kinetic energy level (accompanied by the transition of rotational energy level). Material absorbing electromagnetic radiation should satisfy two conditions: (1) radiation should have the energy just needed to meet the transition of matter; and (2) there is occasional interaction between radiation and matter. When a molecule is irradiated by infrared light with a constant frequency (constant energy), resonance absorption will occur if the vibration frequency of the molecule is consistent with that of the external infrared radiation. Because the atoms of the molecule show different electronegativity due to the different difficulty of gaining and losing valence electrons, the molecule also shows different polarity. These dipoles themselves have some original vibration frequencies. When the external radiation frequencies are the same as the dipole vibration frequencies, the molecules interact with radiation (vibro-coupling). By increasing their vibration energy, the vibration is stimulated and the amplitude is increased, and the molecules transit from the original ground state vibration to a higher vibration level. This frequency range corresponds to energies of about 2–12 kcal/

mol. This amount of energy is sufficient to affect bond vibrations (motions such as bond stretching or bond bending) but is appreciably less than would be needed to break bonds. The second condition for the generation of infrared absorption spectra is that there is a dual interaction between infrared light and molecules. In order to satisfy this condition, the dipole moments of molecules must change when they vibrate. This actually ensures that the energy of infrared light is transmitted to molecules, which is achieved by the change of the molecular vibration dipole moment. Not all vibration will produce infrared absorption, only the vibration of dipole moment changing can cause observable infrared absorption, which is called infrared active vibration; molecular vibration with dipole moment equal to zero cannot produce infrared absorption, which is called infrared inactive vibration. Molecular vibration can be divided into two types: stretching vibration and bending vibration. The former refers to the reciprocating motion of atoms along the bond axis, and the bond length changes during the vibration process. The latter refers to the vibration of atoms perpendicular to chemical bonds. By using infrared spectroscopy, the bond length and bond angle of the molecule can be determined, and the stereo configuration of the molecule can be deduced.

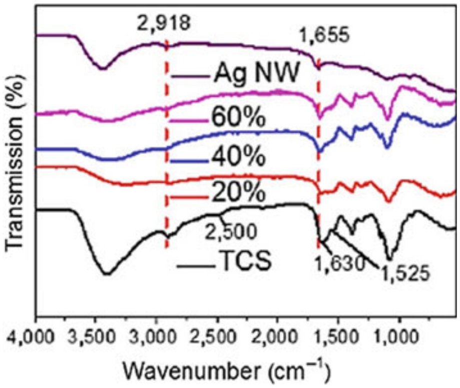
The strength of chemical bonds can be determined by the yield constant. According to the position of absorption peak in the spectrum, the structure of the unknown substance can be inferred, and the content of each component in the mixture can be determined according to the intensity of characteristic absorption peak. Therefore, the main advantage of infrared spectroscopy is that it has good characteristics and can even be used to analyze isomers and stereoisomers. Therefore, it is mainly used for qualitative analysis. The application of infrared spectroscopy has a wide range, but its limitations are lack of sensitivity, difficulty in trace analysis and poor quantification. The interpretation of spectra relies mainly on experience.

FTIR instrument has the advantages of high signal-to-noise ratio, high energy output, high wavenumber accuracy, wide-band measurement range and fast scanning. Therefore, it has a special important position in the analysis of polymer materials. Infrared spectroscopy is often used to identify polymers because of its simple operation and strong spectral characteristics. Infrared spectroscopy can distinguish not only different types of polymers, but also some polymers with similar structures.

IR can be used to characterize different chemical functional groups of silver/polymer nanocomposites. Each polymer has different chemical structure, so their corresponding chemical bond types are different, so different polymers have characteristic infrared absorption spectra, just as everyone is a special existence, no two are exactly the same. Atoms that make up chemical bonds or functional groups are in a state of constant vibration, and their vibration frequencies are comparable to those of infrared light. Therefore, in infrared spectroscopy, when a certain frequency of infrared light irradiates the polymer, its energy will be absorbed by chemical bonds with the same vibration frequency in the molecule. If the vibration frequency of chemical bonds in the molecule is different from that of infrared light, its energy will not be absorbed by the polymer. The vibrational frequencies of chemical bonds in molecules are different. Therefore, according to the absorption spectra of polymers to continuous infrared light, the characteristic chemical groups and their chemical bond types of polymers can be analyzed, so as to judge the chemical structure and distinguish different polymers. In the analysis of polymer spectrogram, the position of the peak, i.e. the characteristic vibration frequency of the band, should be taken into account in the analysis of chemical bond type, which is the basis for qualitative analysis of functional groups. The type of polymer can be determined according to the position of the characteristic peaks. In the infrared spectra of polymers, the bands with the strongest absorption often correspond to the absorption of their main groups, and have certain characteristics. At the same time, each absorption band in the infrared spectra represents a certain vibration form of an atom group or group in the compound. Their vibrational frequencies (corresponding to the wave numbers of absorption bands appearing on the spectra) are directly related to the atomic mass and the strength of chemical bonds in the groups. Of course, they are also indirectly affected by different adjacent structures and chemical environments. For example, in silver/graphene oxide hydrogels, graphene oxide absorptions in infrared spectra is corresponds to the stretching vibration energy of oxygen-hydrogen bond, the vibration energy of carbon-oxygen double bond and the vibration energy of carbon-carbon double bond and carbon-oxygen single bond, respectively. When the content of silver nanoparticles increased, the absorption peak intensity of infrared spectra changed obviously, which indicated that silver nanoparticles reacted with graphene oxide.

Infrared spectroscopy can also be used to characterize the formation mechanism of silver nanoparticles and identify the formation of new chemical bonds. A simple semi-quantitative prediction of the sequence structure of copolymer can be made by characterizing the change of the signal intensity of the absorption peak of a chemical bond in the infrared absorption spectra of polymers, according to the transfer of the absorption peak and the inference of the reaction mechanism in the synthesis. In addition, another important basis for the analysis of infrared spectra of polymers is the band. The band form includes information on whether the band is split or not. It can be used to study the existence of association in molecules and the symmetry, rotational isomerization and tautomerism of molecules. The intensity of the band is related to the change rate of the dipole moment when the molecule vibrates, but it is also proportional to the molecule content, that is, the stronger the band, the more the molecule content. Therefore, it can be used as the basis of quantitative analysis. The dynamic process of polymer formation can be studied according to the change of the intensity of some characteristic bands with time. As shown in Fig. 6, the absorption peak of carbon-oxygen double bond in pure mercapto-chitosan is 1630 cm^{-1}, the absorption peak of carbon-oxygen double bond turns to 1655 cm^{-1} in silver/chitosan polymer films, which is caused by the electron departure effect of silver nanoparticles. Moreover, with the increase of the content of silver nanoparticles, the absorption peak of silver nanowires sulfhydryl chitosan polymer in infrared spectra becomes more and more flat, the peak band becomes wider, and the peak strength decreases. The disappearance of sulfur-hydrogen bond vibration in silver/chitosan polymer films shows that

Fig. 6 FT-IR spectra of Ag NWs, pure TCS, and Ag NW-TCS composite films with different Ag NW contents. Reproduced from Ref. Pan et al. (2018) with permission



silver-sulfur covalent bonds are formed on the surface of silver nanoparticles and sulfhydryl chitosan. The reason is that the organic mercaptan molecule absorbs silver nanoparticles to form a covalent bond between silver and sulfur, which results in the red shift of the corresponding absorption peak band (Pan et al. 2018). Red-shift refers to the movement to the red band, that is, the energy of photons becomes lower, the wavelength increases and the wavenumber decreases, so moving to the low wavenumber is red shift, and vice versa is blue shift. Infrared spectroscopy is a vibration spectroscopy, which usually requires very low energy. Moving to low wave number means that the energy required for vibration is lower and the group is more unstable. The formation mechanism of silver/polymer can be inferred by the change of absorption peak intensity in infrared spectra, and the formation of new chemical bonds can be judged.

3 Scattering Methods for the Analysis of Silver/Polymer Nanocomposites

X-ray is the light radiation produced by the transition of the inner electrons of an atom under the bombardment of high-speed moving electrons. XRD is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of materials. Crystals can be used as gratings for X-rays. The coherent scattering of these large numbers of particles (atoms, ions or molecules) will interfere with light, thus enhancing or weakening the intensity of scattered X-rays. Because of the superposition of scattering waves of a large number of particles, the maximum intensity of the beams produced by mutual interference is called X-ray diffraction lines. By analyzing the diffraction patterns, we can obtain information about the composition of materials, the structure or morphology of atoms or molecules in materials. The crystal structure causes the incident X-ray beam to diffract in many specific directions. By measuring the angle and intensity of these diffracted beams, crystallographers can generate three-dimensional images of electron density in crystals. Based on this electron density, the average position of atoms in crystals, their chemical bonds and other information can be determined.

X-ray is a kind of electromagnetic wave with very short wavelength (about 20–0.06 Å). It can penetrate a certain thickness of substances, and make fluorescent substances emit light, photographic latex sensitizes light, and gas ionizes. X-rays produced by bombarding metal targets with electron beams contain X-rays with specific wavelengths corresponding to various elements in the target, which are called characteristic (or marking) X-rays. X-ray is the light radiation produced by the transition of atom inner electrons under the bombardment of high-speed moving electrons. There are two main types: continuous X-ray and characteristic X-ray. Crystals can be used as gratings for X-rays. The coherent scattering of these large numbers of particles (atoms, ions or molecules) will interfere with light, thus enhancing or weakening the intensity of scattered X-rays. Because of the superposition of scattering waves of a large number of particles, the maximum intensity of the beams produced by mutual interference is called X-ray diffraction lines. XRD is based on the coherent scattering of X-rays and the Bragg formula $2d\sin\theta = n\lambda$, crystal theory and reciprocal lattice Ewald diagram. The basic conditions of diffraction are: (1) the integral multiple of the spacing between layers and the radiation wavelength; (2) the spatial distribution of scattering centers is regular. Main Measurements: Crystal structure information. The main methods include X-ray powder diffraction and single crystal diffraction.

XRD is mainly used to analyze the composition, size and crystallinity of nanoparticles by comparing with standard spectra. With the aid of X-ray diffractometer and the diffraction effect of microcrystalline on X-ray, the diffraction pattern of the sample, i.e. the relationship between the diffraction intensity and the diffraction angle can be obtained. The analysis of its diffraction patterns can be used to investigate the properties of chemical bonds and the relationship between structure and properties. It is a means to obtain information about the composition of materials, the structure or morphology of atoms or molecules in materials. At the same time, it can be applied to the structure analysis of crystallization analysis. From the Bragg formula and the known wavelength λ, the angle of θ can be measured, and the spacing d between crystals can be calculated. Given the d value, θ can be measured to calculate the characteristic radiation wavelength and determine the elements contained in the sample. Particle size can be estimated also. According to the spectral line width and the calculation formula, the average grain size can be calculated.

At present, X-ray diffraction (including scattering) has become an effective method to study the microstructures of crystalline and some semi-crystalline materials. For the application of silver/polymer nanocomposite, XRD can be used in chemical analysis, i.e. qualitative and quantitative analysis, which is a widely used aspect of X-ray diffraction in polymer. For qualitative analysis, by comparing the X-ray diffraction of polymer composites before and after the chemical reaction, one can analyze the diffraction spectrum, comparing the differences of the diffraction peaks to check whether there are new diffraction peaks. If new diffraction peaks appear, silver nanoparticles might be generated in the polymer matrix, otherwise there will be no silver nanoparticles. If there is no load of silver nanoparticles, there is no characteristic peak in the spectra which could be used to verify the existence of silver nanoparticles. For the quantitative analysis of silver/polymer nanocomposites, each element has its own special diffraction peaks, and the corresponding peaks of silver with different content are different. The area under the general diffraction peaks represents the content of the element. By analyzing the intensity of the diffraction peaks, we can roughly determine the content of silver nanoparticles and determine the content of silver nanoparticles in materials (Fig. 7).

X-ray diffraction can also be used for phase analysis of silver/polymer nanocomposites. General chemical analysis is used to analyze the kinds and contents of the elements in the constituent substances, but the internal structure of the polymer composite cannot be analyzed. Phase analysis can provide the state of chemical bonding between elements and the aggregation structure of substances. The chemical composition can be same, but the chemical bonding state or aggregation state of substances can be different. As in the case with SiO_2, amorphous silica gel, crystalline quartz and white silica can be formed due to different aggregates. For silver/polymer nanocomposite, the chemical bonds formed by silver nanoparticles may be different in different polymers, thus, the aggregation states are different, and the ways in which silver nanoparticles linked with polymers are different. When X-ray diffraction scans over silver/polymer nanocomposites, the

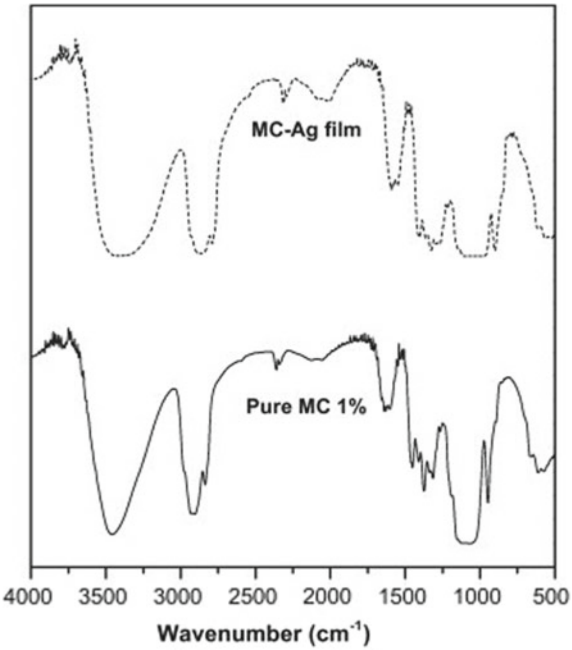


Fig. 7 FTIR spectra of methylcellulose (MC) and methylcellulose–silver (MC–Ag) nanocomposite film. Reproduced from Ref. Maity et al. (2012) with permission

characteristic peaks of silver nanoparticles can be obtained in the spectra. Different silver phase will lead to different characteristic peaks, and the corresponding angles are also different. The appearance of those X-ray diffraction peaks essentially represents the existence of different crystalline structure, that is, the substance is crystalline. According to the diffraction spectra, the diffraction peaks formed by silver nanoparticles at different angles can be used to infer the crystal planes of silver nanoparticles in polymers, and to better understand the phase of silver nanoparticles in polymers. For example, silver nanoparticles in poly(vinylidene fluoride) and in polydopamine matrix, four characteristic peaks corresponding to 38.150, 44.194, 64.156 and 77.624 degrees of silver nanoparticles can be observed (Fig. 8). The corresponding characteristic peaks of PVDF are 20.08, 36.34, and 40.56 degrees. And the poly(vinylidene fluoride) shows a single peak at 20.5 and 38.8 degrees, corresponding to the [110] and [200] planes and the [002] planes, respectively (Zhang et al. 2015). The plane of silver nanoparticles corresponding to different bond angles was characterized. The orientation of silver nanoparticles in polymer can be well analyzed by X-ray diffraction, and the three-dimensional structure of silver nanoparticles can be understood.

In another case, when ammonia water is added into silver nitrate solution, silver-ammonia complexes begin to form. When graphene oxide is added, silver-ammonia complexes are easily absorbed into oxygen-containing functional groups with negative charges on graphene oxide because of the positive and negative phase absorption of charges. With the addition of glucose, silver-ammonia complex was reduced to silver nanoparticles by aldehyde group of glucose. The characteristic peaks of silver nanoparticles appeared in the related XRD spectra, which proved the formation of silver nanoparticles, explained the formation mechanism of silver nanoparticles polymer. Therefore, reaction process between silver nanoparticles and polymer can be speculated (Fan et al. 2014).

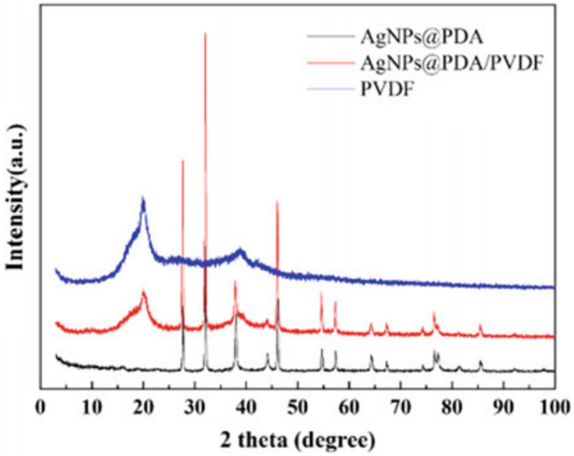


Fig. 8 XRD patterns of Ag nanoparticles@polydopamine (AgNPs@PDA) particles, poly(vinylidene difluoride) (PVDF) film, and AgNPs@PDA/PVDF composite film. Reproduced from Ref. Zhang et al. (2015) with permission

In summary, the application of XRD in silver nanoparticles polymer is very extensive. It can not only qualitatively and quantitatively analyze silver nanoparticles, but also analyze the internal chemical structure of silver nanoparticles polymer, and characterize the corresponding crystal planes of silver nanoparticles at different angles. At the same time, it has a good tool to speculate formation mechanism in silver/polymer nanocomposite.

Laser particle size analyzer is an instrument that used to analyze particle size by means of diffraction or spatial distribution of scattered light (scattering spectrum). It is characterized by fast test speed, wide test range, good repeatability, easy operation and so on. It can be divided into static light scattering (SLS) and dynamic light scattering (DLS) laser particle size analyzer. The SLS is mainly suitable for testing micron particles. The size of nanoparticles can be analyzed by detecting the dynamic light scattering signals of one or two scattering angles according to the Brownian motion of particles. The data obtained is the average particle size.

The diffusion coefficient is inversely proportional to the particle size according to the Stokes Einstein equation. Photonic correlation spectroscopy (PCS) is a technique that used to determine the diffusion coefficient of small particles in liquid by accurately measuring the light scattering intensity of particles as a function of time. When the particles are small, the particles in the liquid are affected by Brownian motion and show a random motion state. When the laser is irradiated onto these particles, the laser light scatters in all directions. The wave frequency of the scattered light contains the information of the particle size. For larger particles that move more slowly, the fluctuations will be slower. When the beam is blocked by particles, part of the light will be scattered. The scattering light will travel at an angle of theta to the direction of the main beam. Scattering theory and experiments show that theta is related to the size of the particle, and the larger the particle, the smaller the scattering light. The smaller the particle, the greater the theta angle of the scattered light. The scattered light is collected at a selected angle and measured by a highly sensitive detector.

Figure 9 shows TEM images and DLS analysis results. The particle size distribution of the prepared nanoparticles is narrow, spherical and pseudo spherical. In DLS analysis (inset), silver nanoparticles exhibit peaks centered at 98 nm in the sample. These results confirm the good stability of gallic acid for nanoparticles (Espinosa-Cristóbal et al. 2009).

Zeta potential is an important characterization parameter of nanomaterials. The net charge on the surface of particles affects the distribution of ions in the region around the particle interface, which leads to the increase of the concentration of counter ions close to the surface. Therefore, there are electric double layers around each particle. There are two parts in the liquid layer around the particles: one is the inner layer, which is called Stern layer, in which the ions are tightly bound to the particles; the other is the outer dispersion area, in which the ions are less closely adsorbed on the particles. In the dispersion layer, there is an abstract boundary, in which ions and particles form stable entities. When a particle moves (e.g. due to gravity), ions within this boundary move with the particle, but ions outside the

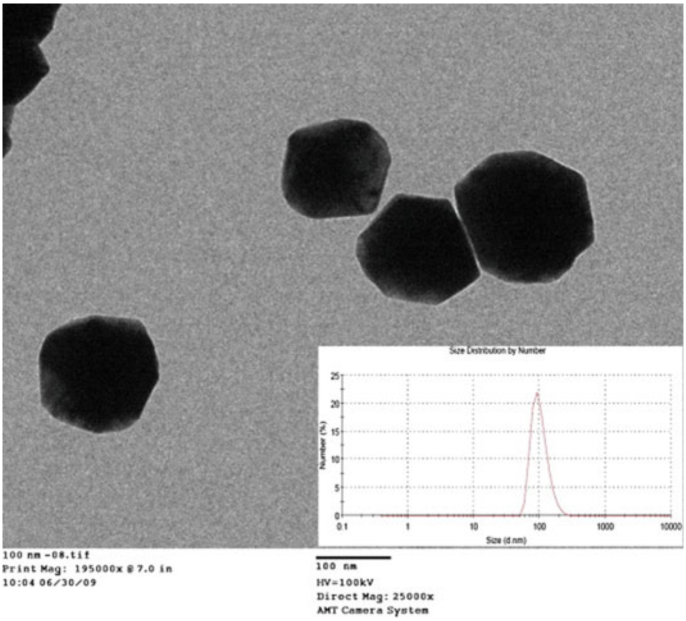


Fig. 9 TEM and DLS results of the silver nanoparticles prepared by the addition of gallic acid to $AgNO_3$ solution method. The mixture was irradiated with UV light (254 nm, 15 W) during 30 min. Reproduced from Ref. Espinosa-Cristóbal et al. (2009) with permission

boundary do not. This boundary is called a hydrodynamic shear layer or sliding plane. The potential at this boundary is called zeta potential.

Zeta potential can be used as an indicator of the stability of colloidal system. If the particles have a lot of negative or positive charges, that is, very high zeta potential, they will repel each other, so as to achieve the stability of the whole system; if the particles have few negative or positive charges, that is to say, their zeta potential is very low, they will attract each other, thus reaching the instability of the whole system. Generally speaking, the higher the zeta potential is, the more stable the dispersion system is. The dividing line of particle dispersion stability in aqueous phase is considered at +30 mV or −30 mV. If all particles have zeta potential higher than +30 mV or lower than −30 mV, the dispersion system should be relatively stable.

Zeta potential of dispersion system can be changed by the following factors: pH, conductivity of solution and the concentration of a particular additive, such as surfactant, polymer. The stability of the product can be obtained by measuring zeta potential energy of a particle as the above variables, and in turn, the best conditions for flocculation can be determined.

For instance, Sankar et al. formulated the biodegradable poly-D, L-lactide-co-glycolide (PLGA) polymer based biogenic silver nanocomposite by modified solvent casting method. The zeta potential value of Ag NPs was −33 mV with

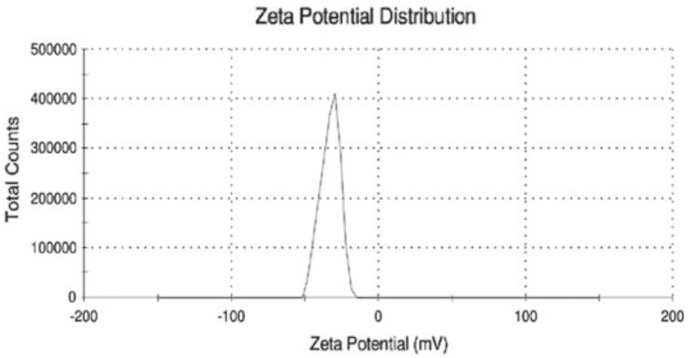


Fig. 10 Zeta potential measurement of Ag NPs. Reproduced from Ref. Sankar et al. (2016) with permission

average particle size distribution was 115 nm (Fig. 10). It is well accepted that a zeta potential value of about −25 mV approves a high energy barrier for the stabilization of nano suspension (Sankar et al. 2016).

4 Silver/Polymer Nanocomposites: Thermal Characterization

Thermal gravimetric analyzer (TGA) is a kind of instrument which uses thermogravimetric method to detect the relationship between temperature and mass of substances. TGA is to measure the change of mass of substance with temperature (or time) under programmed temperature control, in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The important characteristic of thermogravimetric method is that it has strong quantification and can accurately measure the change of mass and the rate of change. It can be said that as long as the change of mass occurs when the material is heated, the thermogravimetric method can be used to study the change process.

When the substance under test sublimates, vaporizes, decomposes into gas or loses crystalline water during heating, the quality of the substance under test will change. At this point, the thermogravimetric curve is not a straight line, but a decline. By analyzing the thermogravimetric curves, we can know how much the measured substance changes at different degrees. According to the weight loss, we can calculate how much substance has been lost. The thermogravimetric analyzer is mainly composed of balance, furnace, and temperature control system by program and recording system.

There are two commonly used measuring principles: displacement method and zero-position method. The so-called displacement method is based on the proportional relationship between the inclination of the balance beam and the change of mass, using differential transformer to detect the inclination, and automatically record it. Zero-position method is to use differential transformer method and optical method to measure the inclination of balance beam, and then to adjust the current of coil installed in balance system and magnetic field, so that the coil rotation restores the inclination of balance beam, that is, the so-called zero-position method. Since the force exerted by the coil rotation is proportional to the change of mass, and this force is proportional to the current in the coil, the curve of mass change can be obtained by measuring and recording the change of current. The most widely used TGA method is based on continuous measurement of weight on a sensitive balance (called a thermobalance) as sample temperature is increased in air or in an inert atmosphere. Data are recorded as a weight loss versus temperature.

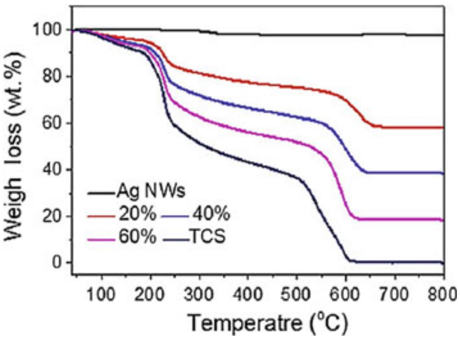
The important characteristic of thermogravimetry is that it can measure the change of mass and the rate of change accurately. The main measurement is the decomposition temperature of the material. The temperature at which the general mass loses 95% is denoted as the decomposition temperature normally.

Thermogravimetric analysis can study the changes of crystal properties, such as the physical phenomena of melting, evaporation, sublimation and adsorption, the thermal stability, decomposition process, dehydration, dissociation, oxidation, reduction, quantitative analysis of components, the influence of additives and fillers, water and volatiles, reaction kinetics and other chemical phenomena. The TGA curve takes mass as ordinate, decreases mass from top to bottom, temperature (or time) as abscissa, and increases temperature (or time) from left to right. TGA is mainly the relationship between temperature e and mass, so temperature has a great impact on the measurement. The higher the heating rate, the greater the impact it will be. With the increase of heating rate, both the starting and ending temperatures of decomposition increase correspondingly, but the weight loss is not affected by heating rate. With different heating rates, the shape of TGA curve changes, the heating rate increases and the resolution decreases, this is not good to the detection of intermediate products. After the TGA curve is finished, the weight loss percentage of each temperature range can be calculated according to the amount of original sample and the weight loss of each temperature range. It is used to study the thermal stability and composition of materials. Generally, there are several methods to judge the thermal stability of materials. Firstly, the direct comparison the TGA curves of several materials on the same drawing to make an intuitive comparison. Secondly, stipulates a temperature value and then calculates the weight loss percentage at this temperature. The greater the weight loss, the worse the thermal stability of the material will be. Thirdly, the method of constant weight loss temperature stipulates a percentage of weight loss and calculates the corresponding temperature. The higher the temperature, the better the thermal stability will be. Or it can be judged by the starting and ending temperatures of material weightlessness. The higher the starting and ending temperatures, the better the thermal stability will be.

TGA can be used to determine the thermal stability of silver/polymer. TGA has strong quantification and can accurately measure the change of mass and its rate of change, whether the change is chemical or physical, so it is the most widely used analytical technique for the analysis of polymer content, as shown in Fig. 11. The mass loss of silver nanoparticles varies with the content of silver nanoparticles in polymers when TGA is run at the same temperature. In the TGA curve, the load of silver nanoparticles can be analyzed by observing the mass loss of polymers with different silver nanoparticles content. The temperature value on the weight loss curve is used to compare the thermal stability of materials. The thermal stability of silver nanoparticles polymers with different content is different. According to the different decomposition temperature of polymers, the influence of silver nanoparticles content on the thermal stability of polymers can be judged. For example, in silver/chitosan polymers, the mass of silver nanoparticles is not lost when the temperature changes, while the mass of mercapto-chitosan is greatly lost. As shown in Fig. 11, when the silver nanoparticles are assembled into the polymer, the mass loss of the mercapto-chitosan polymer is obviously reduced. When the content of silver nanoparticles is more and more, the mass loss of the polymer is less and less. It shows that the thermal stability of the polymer increases with the increase of silver nanoparticles content (Pan et al. 2018). TGA can be used in combination with differential thermal analysis to better judge the thermal stability of silver nanoparticles polymer, and can also speculate whether there are impure substances.

Differential Thermal Analysis (DTA) utilizes a reference sample which does not undergo any chemical reaction and physical change at a certain experimental temperature to compare with an equal amount of unknown sample in the same environment. Any chemical and physical changes of the unknown substance will increase or decrease temporarily compared with the temperature of the reference sample in the same environment. The decrease is endothermic reaction and the increase is exothermic reaction. When the unknown sample and the reference sample are given the same temperature, the rise of temperature for both the samples will be different because of their different thermal properties. The purpose of the analysis is to measure the temperature difference between them. The curve obtained by taking the temperature difference between the reference material and the sample as the

Fig. 11 TGA of silver nanowires (Ag NWs) and different doping ratio with TCS. Reproduced from Ref. Pan et al. (2018) with permission



longitudinal coordinate and the temperature as the abscissa coordinate is called DTA curve. When analyzing the thermal stability of silver/polymer composite, two different curves were obtained when the thermogravimetric analyzer and differential analysis were used together. By comparing the different temperatures corresponding to the mass loss of silver/polymer in the two curves, the thermal stability of polymer can be inferred. For example, in silver/cellulosic, the mass loss temperature of cellulose is at about 250–260 degrees. The main mass loss temperature ranges from 370 to 410 degrees which is due to the degradation of organic substances in the composites, which is much higher than the decomposition temperature of cellulose itself. It is shown that the thermal stability of the material is enhanced when the silver/cellulose composites is formed. At the same time, it was also observed that the mass loss of silver/cellulose polymer composite occurred between 300 and 320 degrees, which is possibly due to the decomposition of other impurities. Through mass loss, it can be inferred whether there are other impurities in the polymer, and the purity of the polymer can be qualitatively judged (Maleki et al. 2017). As shown in Fig. 12, the pure and 1% Ag doped CdO examples in the TG-DTA curve show that the decomposition peak/melting temperature is 208 and 105°C, corresponding mass loss is 9% and 7%, respectively, as shown in the first step of the curve. In the second step, the organic decomposition temperature of the pure sample and the silver-doped sample were 333 and 233°C respectively, and 6% and 8% mass were lost respectively. This result shows that the percentage of organic decomposition increases from pure silver to silver doped (2%). Step 3: DTA curve shows the inorganic decomposition of 1% Ag doped samples at 380, 384 and 373°C, and the mass loss corresponding to TG curve is 2% respectively (Sivakumar et al. 2015).

Differential scanning calorimetry (DSC) is a thermos analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature programed for a DSC analysis is designed so that the temperature of sample holder increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to

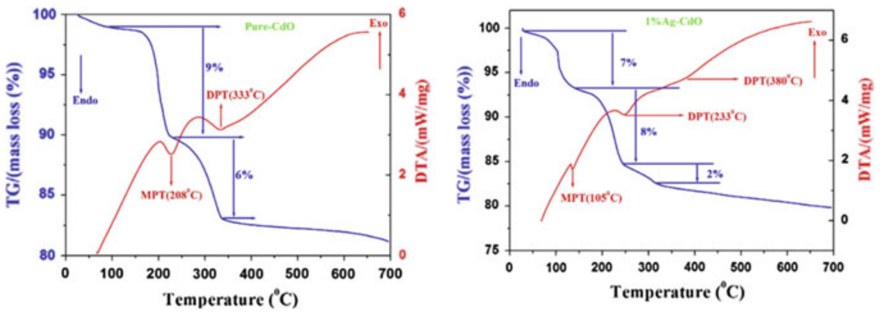


Fig. 12 TG–DTA curve for pure-CdO and 1% Ag-CdO nanoparticles. Reproduced from Ref. Sivakumar et al. (2015) with permission

be scanned. Since DSC can measure a number of characteristic properties of a sample, like glass transition, heat capacity and crystallization temperature, DSC is used widely for examining polymeric materials to determine their thermal transitions. Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show polymer degradation by the lowering of the expected melting point, T_m, for example. T_m depends on the molecular weight of the polymer and thermal history, so lower grades may have lower melting points than expected. The percent crystalline content of a polymer can be estimated from the crystallization/melting peaks of the DSC graph as reference heats of fusion can be found in the literature. DSC can also be used to study thermal degradation of polymers using an approach such as Oxidative Onset Temperature/Time (OOT).

Satyendra Mishra et al. synthesized the highly stable, semicon-ducting polyaniline/silver nanocomposites which are prepared in situ by employing the acoustic cavitation mechanism to obtain the composite in nanophase. Phase transitions were investigated over the range of 35–300 °C at 10 °C/min under nitrogen atmosphere on a DSC 60 differential scanning calorimeter. TGA and DSC results indicated greater thermal stability for the nanocomposites along with higher crystallinity (Mishra et al. 2012). Mohammad et al. reported an nanocomposites of poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogels with silver nanoparticles (Ag NPs). The DSC experiments was found to vary with conversion in a different way compared to neat PHEMA (Siddiqui et al. 2016).

5 Mechanical and Viscoelastic Characterization of Silver/Polymer Nanocomposites

Dynamic mechanical analysis (DMA) is a technique that used to study the viscoelastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus. This approach can be used to locate the glass transition temperature as well as to identify transitions corresponding to other molecular motions of the material.

Lavinia Balan et al. reported a new method for the preparation of silver nanoparticles/polymer nanocomposite materials by UV-radiation curing of multifunctional acrylate monomers. Silver nanoparticles possessing an average diameter of 6.6 nm were first prepared by chemical reduction of silver nitrate with *t*-BuONa-activated sodium hydride in THF. The viscoelastic properties of the nanocomposite were monitored by DMA (Fig. 13). Silver nanoparticles were found to have no detrimental effect on the photopolymerization kinetics and the incorporation of metal nanoparticles allowed to reduce the gloss of UV-cured coatings. An increase of the diameter of silver nanoparticles to 20 nm was observed during the curing process (Balan et al. 2008).

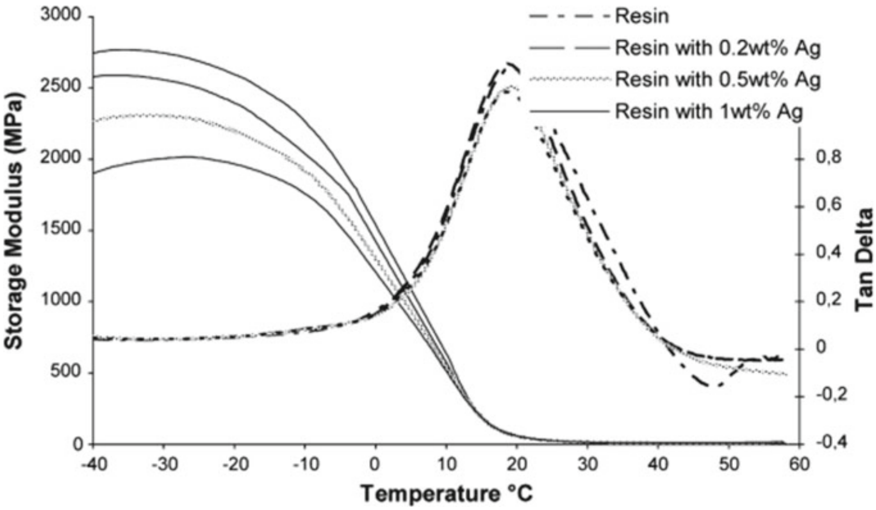


Fig. 13 Influence of silver nanoparticles on the viscoelastic characteristics and tan δ profiles recorded by DMA for a UV-cured polyurethane-acrylate. Reproduced from Ref. Balan et al. (2008) with permission

Antoine Lonjon et al. prepared highly conductive composites of silver nanowires and semicrystalline polyamide 11 for different content. DSC and DMA have shown high stability of the composite physical structure and an optimization of the mechanical properties as a function of nanowires content of 3.6 vol.%. A simultaneous enhancement of the electrical conductivity of polyamide 11 was also obtained (Lonjon et al. 2013).

Different chemical structures of polymers can be designed and synthesized to produce polymers with different glass transition temperature (T_g), melting temperature (T_m), crosslinking, and crystallinity that will result in different mechanical behaviors. Usually, polymers are used as matrix materials, which requires that they have good mechanical properties, durability and adaptable to various needs (e.g. as fibers to withstand tension; as plastic products to withstand knocking; as rubber to be elastic and wear-resistant, etc.). Mechanical properties refer to the mechanical responses of materials after being subjected to force, such as deformation, reversibility of deformation and damage resistance. These responses can be expressed by some basic parameters.

The mechanical properties of polymers indicate the relationship between stress and strain of polymers under external forces. When polymers are used as structural materials, their mechanical properties are particularly important, basic parameters of mechanical properties including strain and stress plot, elastic modulus, hardness and strength.

Polymer materials are viscoelastic. When the stress is removed, part of the work is used for frictional effect and converted into heat energy. This process can be expressed by stress-strain curve. The abscissa of the curve is strain, and the longitudinal coordinate is external stress. The shape of curves reflects various deformation processes such as brittleness, plasticity, yield and fracture of materials under external forces. This stress-strain curve is usually called engineering stress-strain curve. It is similar to the load-deformation curve, except that the coordinates are different.

Stress is usually expressed as changes in unit length (area, volume). When the material is deformed under the action of external force, the additional internal force against external force will also be generated in order to keep the material in its original state. When the external force is eliminated, the internal force will make the material return to its original state and gradually eliminate itself. When the external force is in balance with the internal force, the internal force and the external force are equal in size and opposite in direction. Internal force per unit area are defined as stress.

Strain is the relative change in shape or size of an object due to externally-applied force. When a material is loaded with a force, it produces a stress, which then causes a material to deform. Engineering strain is defined as the amount of deformation in the direction of the applied force divided by the initial length of the material.

Stress-strain curves are most commonly used to describe the mechanical properties of polymers. Its shape depends on the polymer's chemical structure, physical structure, experimental conditions, chemical composition, structure, molecular weight and its distribution, polymer branched bonding, crystallization and orientation, size and shape of crystal region, processing state, temperature, rate and so on, which will affect the distribution of stress-strain curve of polymer. According to these characteristics, stress-strain curves can be divided into the following categories. (1) The material is hard and brittle: under the action of larger stress, only minor strain occurs, and fracture occurs before yield point. It has high modulus and tensile strength, but the stress is brittle fracture, and the impact strength is poor. (2) Material is hard and strong: under greater stress, the material has smaller strain, breaks near the yield point, has high modulus and tensile strength. (3) Material is strong and tough: has high modulus and tensile strength, fracture elongation is larger, when the material is subjected to force, it belongs to ductile fracture material: low modulus, low yield strength, high fracture elongation, high fracture strength, can be used for demanding deformation. (4) Soft and weak materials: low modulus, low yield strength, medium breakage, crack elongation. (5) Weak and brittle materials: generally, oligomers, it cannot be directly used as materials.

The mechanical properties of polymer composites depend on different parameters. The intrinsic properties of polymer composites have great influence on the mechanical behavior of hydrogen bond, van der Waals force and covalent bond, and these chemical bonds and intermolecular forces will ultimately affect the mechanical properties of polymer. For the characterization of mechanical properties of silver/polymer nanocomposites, the stress-strain curves were used to analyze. In the stress-strain curve, the mechanical properties of silver nanocomposites are related to the formation of new chemical bonds and the content of silver nanoparticles in the polymer. Silver nanocomposites exhibit excellent mechanical properties because of the formation of chemical bonds between silver nanoparticles and the polymer matrix. Moreover, the curves of different silver nanoparticles are changed. When the content of silver nanoparticles changes, the strain decreases and the stress increases, this indicates that the mechanical properties of the polymer increase. If the stress decreases and the strain increases, the mechanical properties of the polymer decrease. The mechanical properties of mercapto-chitosan with silver nanoparticles are higher than that of chitosan because disulfide bonds are formed when silver nanoparticles form polymers with chitosan, which leads to the increase of mechanical properties (Pan et al. 2018). The mechanical properties of the polymer vary with the content of silver nanoparticles. When the content of silver nanoparticles increases, very small strain occurs in the polymer under great stress, which indicates that the mechanical properties of the polymer are enhanced with the increase of the content of silver nanoparticles.

The tensile strength of silver nanoparticles can be characterized as explained below. When the material is subjected to external forces that exceed the material's bearing capacity, the material will be destroyed. Mechanical strength is a measure of material's ability to resist external forces, which means the maximum stress that material can bear under certain conditions. Tensile strength measures the ability of materials to resist tensile damage. Stress-strain curve can also characterize the tensile strength of a polymer. When the stress of a polymer is larger and the strain is smaller, hence the tensile strength of polymer is higher. Silver nanoparticles can enhance the ultimate mechanical properties of polymer, so the more the content of silver nanoparticles, the greater the mechanical properties of polymer, the corresponding tensile strength of polymer is enhanced. As shown in Fig. 14, when the content of silver nanoparticles in mercapto-chitosan polymer increases, the tensile strength of the polymer increases gradually. When the content of silver nanoparticles increased to 70%, the tensile strength of the polymer will decrease. The reason is that when the content of silver nanoparticles is too high, silver nanoparticles will gather on the surface of the polymer, resulting in poor dispersion of silver nanoparticles. Therefore, the tensile strength of the compound decreases (Pan et al. 2018).

Elastic modulus and toughness are also important basis for characterizing the mechanical properties of polymers. Modulus refers to the magnitude of stress required per unit strain in the range of elastic deformation. It is a characterization of

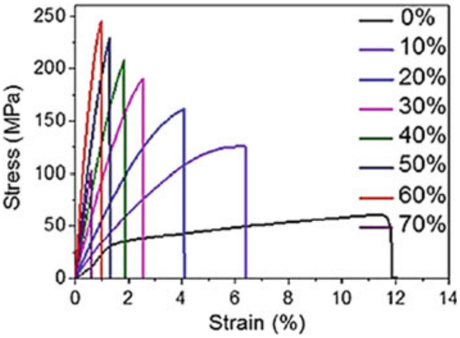


Fig. 14 Stress–strain curves of a series of Ag NW-TCS composite films with increasing Ag NW content. Reproduced from Ref. Pan et al. (2018) with permission

material rigidity. For ideal elastic solids, the relationship between stress and strain obeys Hooke's law, that is, stress is proportional to strain. The proportional constant is called modulus of elasticity, or modulus for short. Elastic modulus characterizes the material's resistance to deformation. The greater the modulus, the less easy it is to deform, and the greater the stiffness of the material. Toughness, a physical concept, represents the ability of a material to absorb energy during plastic deformation and fracture. The better toughness, the less possibility of brittle fracture will be. Toughness can be found in materials science and metallurgy. Toughness refers to the resistance of a material to fracture when subjected to forces that deform it. It is defined as the ratio of energy absorbed by a material to its volume before fracture. When the content of silver nanoparticles reaches 60%, the mechanical properties of silver nanocomposites are the largest. The elastic modulus and toughness of silver nanocomposites are 32.8 GPa and 1.4 MJ/m^3, which are many times higher than those of polymer composites without doping. Moreover, the fracture surface of Ag/polymer is very irregular and trapezoidal (Pan et al. 2018).

In the application of silver/polymer nanocomposites, one of the most important properties is that they are durable and have good toughness. Therefore, the fatigue resistance of polymers will be tested before they are used. Fatigue strength refers to the maximum stress of materials under infinite alternating loads without damage, which is called fatigue strength or fatigue limit. In the fatigue test of silver/polymer nanocomposites, the fatigue strength of the polymer was observed by multiple strains. Whether the polymer could be reduced to its original shape after strain, the more the cycle times, the weaker the reduction degree of the polymer. Recording the reduction times of polymer fracture can effectively characterize the fatigue strength of the composites. For example, in silver/mercapto-chitosan, the strength of the polymer decreased slightly. After 100 bending experiments, the fatigue resistance of the polymer was very high (Pan et al. 2018).

Different polymers have their unique mechanical properties. Stress-strain curves, Young's modulus, tensile strength and hardness are important parameters to characterize the mechanical properties of materials. Therefore, by analyzing these parameters, we can explore how silver nanoparticles affect the mechanical properties of polymer and judge the strength of the mechanical properties of silver/polymer composites.

6 Conclusion

Various commonly used characterization methods and recent progress towards silver/polymer composites include SEM, TEM, EDX, XRD, XPS, IR, UV-vis, TGA, DTA, DMA and characterization of mechanical properties, through which the morphology, microstructure, elemental composition, mechanical properties and thermal properties of have been explained and analyzed in this chapter.

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