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Applications of Spectroscopic Techniques for Polymer Nanocomposite Characterization

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Research Article

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Applications of spectroscopic techniques for polymer nanocomposite characterization

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ABSTRACT

During past decades, spectroscopic techniques find wide range of applications ranging from biological applications to the measurement of chemical composition and characterization of variety of substances i.e., polymers, nanocomposites etc. Nanocomposites are emerging and growing materials having wide variety of uses. To study the characteristic properties, characterize, and development of new materials using polymer nanocomposites, several molecular characterization techniques are available and are in use today. Principle objective of this review is to summarize the knowledge in current characterization techniques and to study the applications of fluorescence, solid-state nuclear magnetic resonance (NMR), infrared, besides Raman molecular characterization techniques for characterization of polymers, filler, and composites. Fluorescence technique did not provide detailed analysis of materials while solid-state NMR spectroscopy determine silanol hydroxyl groups at the silica exterior in addition to their interactions with polymer and polymer-filler interfacial interactions (via relaxation time). For characterization of various kinds of functional groups in polymer/ fillers, infrared spectroscopy employed. While Raman spectroscopy finds extensive applications for analysis of carbon-based materials. Novelty of this review is that till yet very few review papers have been published which briefly describe all these mentioned techniques along their applications in a very simple and an effective way.

Keywords: Spectroscopy, Polymer, Nanocomposites, Characterization, Fluorescence, solid-state nuclear magnetic resonance, infrared spectroscopy, Raman spectroscopy.

Vocabulary

Fluorescence: Characterization technique widely used for analysis of exfoliation or intercalation in clay composites.

Nanocomposites: Polymer matrix composites having fillers with at least one dimension less than 100 nm are known as polymer nanocomposites which have properties better than traditional composites.

Solid-state NMR spectroscopy: Analysis tool for characterization of molecular structure, conformation, and dynamics of polymer chains in various kinds of polymer composites.

Infrared spectroscopy: this analysis technique widely used for material characterization via bands/ peaks specific for each functional group of the polymer.

Raman spectroscopy: This technique finds extensive applications for characterization of carbon-based materials via resonance-enhanced scattering effects.

Introduction

Nanomaterials i.e., spheres, sheets, as well as rods etc. spread in polymer materials found numerous applications and study in rubber nanocomposites owing to their improved mechanical, electrical besides thermal characteristics. When these filler elements are spread inside polymer matrix, it resulted in the extraordinary interfacial area amongst organic and inorganic phases and interfacial connections amongst these two phases (governs the level of matrix strengthening) [1]· [2].

Importance of interfacial adhesion besides filler dispersion can be determined through stationary in addition to active mechanical performance. Traditional composites (such as those composites in which silica and carbon black are used as fillers) show upsurge in elastic modulus besides tensile power owing to strong interface whereas feeble interface resulted in intensification of early composite modulus besides insignificant rise in stress. Silica filled hydrocarbon rubber has weak interface which can be improved by using chemical combining vehicle in the packed structure which is responsible for increasing adhesion amongst filler and rubber [3]. Using sol-gel process (hydrolysis in addition to condensation of inorganic alkoxides of metals such as Si, Ti, Al, Zr, Hf, Ta, Sn etc.) nanosized inorganic structures are produced in situ in rubbers, thermoplastics, and thermosets [4]· [5], [6], [7], [8], [9] which resulted in more fine dispersion of mineral phase with composite development possessing outstanding mechanical, thermal and optical characteristics.

To achieve great interfacial region designed for polymer-filler interaction, high level of distribution as well as small sized particles are involved. In poly (dimethyl siloxane) (PDMS) networks, together with silica particles as fillers, polymer-filler interactions are attained by means of hydrogen bonding amongst hydroxyl parts of silica exterior as well as oxygen atoms of polymer chains [10]· [11]. Higher modulus and higher extensibility can be achieved when Silica-titania mixed-oxide fillers are used in PDMS networks as compared with those networks where single filler are used [12]· [13].

Research on composites centered over layered silicates comprised of stacked parts of one to a several nm wide started following manufacturing of nylon 6/ clay nanocomposites by the Toyota Research Group. The purpose behind this is to attain exfoliated structure in which silicate sheets remain evenly spread in host medium [14]· [15], [16], [17]. Exfoliated nanocomposites have the benefit of being utilized in food packing owing to their reduced penetrability to gas and water vapors [18]. In situ polymerization procedure or traditional melt working ways i.e., extrusion or injection molding are useful for preparation of clay nanocomposites. Poor electrical conductivity of clay nanocomposites can be overwhelmed by the addition of conductive insertions (such as small number of carbon-based materials). Physical performance of composite can be improved through two fold filling method such as using spheres besides rods [19], or spheres in addition to plates [20].

As compared to traditional carbon black, carbon nanomaterials, such as carbon nanotubes, graphite or graphene possess excellent electrical conductivity, mechanical power combined with high aspect ratios. Owing to these characteristics, they are known as advanced reinforcing fillers for polymeric metrices. Exceptional structure (made up of cylinders of single or additional graphene layers) of carbon nanotubes (CNTs) make it more useful carbon nanostructure [2]. A lot of work has been performed on methods used for dispersal of CNTs within polymer matrix. Among them calendaring is widely used way, its principle and calendaring mechanism is shown in
Fig. 1. However, various findings showed poor spreading or dispersal of CNTs within polymer matrix (owing to lack of interfacial adhesion in addition to their capacity to pack together. In order to achieve their good dispersion and contact with polymer chains functionalization of tube exterior is carried out [21].

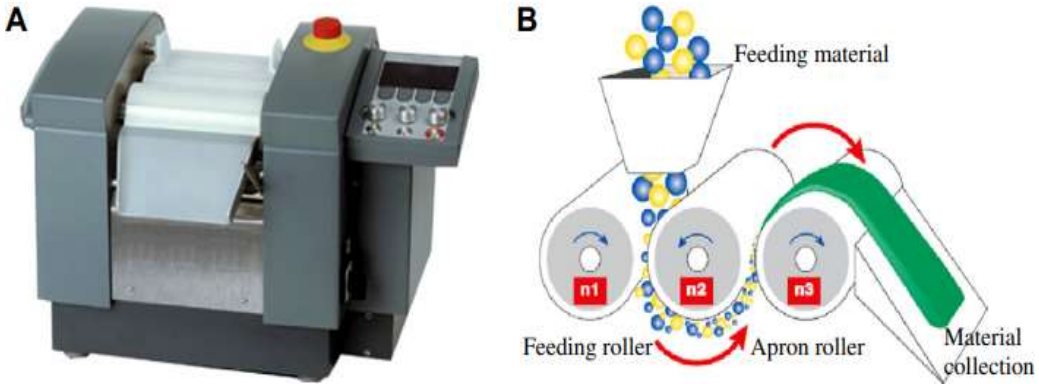


Fig. 1| (A) Calendaring machine for particle spreading into polymer medium (B) Working mechanism of calendaring process (image reprinted with permission) [21].

Punetha et al. debated numerous approaches and practices with their applications for carbon nanomaterials functionalization [22]. Zhang et al. discovered that photochromic molecules, such as use of azobenzenes, diarylethenes, spiropyrans/ oxazines and stilbenes for carbon nanomaterials functionalization is accountable for their additional characteristics [23].

Several techniques have been established intended for attaining sole sheets by means of graphite intercalation compounds. Masses of graphene known as graphite nanostructures or graphite nanoplatelets (GNPs) with 1-10 nm thickness are the result of these techniques. However, Raman spectroscopy showed several structural flaws when chemical alteration of graphite yield graphene. Oxidation of graphite towards graphene oxide after which it reduced to form graphene (a), and mechanism of reduction by hydrazine (b), is shown in

Fig. *2* [24],[25],[26],[27]. Owing to low conductivity, resultant oxidized material is not used as conductive filler. Additional information regarding the production, processing requirements of various graphite nanostructure, and their (graphite-graphene grounded nanocomposites) characterization can be found in literature [28],[29],[30],[31],[32],[33],[34],[35].

Above debate revealed that a complete understanding of the composite and its properties is required before their use and, in this regard, molecular spectroscopy is supportive which offers molecular level characterization. This review article focuses on uses of molecular spectroscopy such as fluorescence, solid-state NMR, infrared, as well as Raman spectroscopy etc. aimed at polymer composite investigation besides quoting examples of the grouping of atomic force microscopy and infrared spectroscopy (AFM-IR) and tip-enhanced Raman scattering (TERS) for the purpose to achieve chemical information with nanometric spatial resolution.

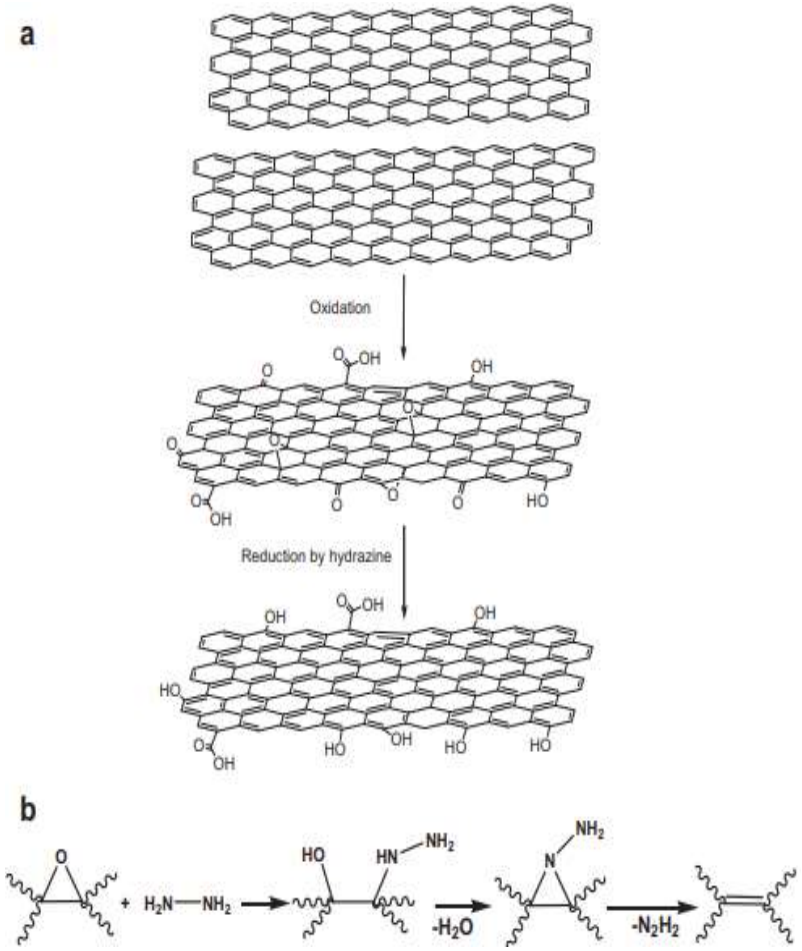


Fig. 2| (a) Graphite oxidation to graphene oxide which is then reduced to form graphene, (b) mechanism of reduction by hydrazine (image reprinted with permission) [24].

Box 1| **unique properties of polymer nanocomposites**

polymer matrix composites having fillers with at least one dimension less than 100 nm are known as polymer nanocomposites. These polymer nanocomposites are of great interest in modern's world owing to several reasons which include:

- These polymer nanocomposites have extraordinary large interfacial area because of their small size as compared to that of traditional composites [36]. Additionally, nanoscale fillers possess characteristics different from that of bulk properties of the same raw material e.g., on reducing size of silicon nanoparticles band gap fluctuate which then particle's color [37].
- Since 100 years, elastomeric composites with nanoscale spherical fillers are employed [38]. In the past 15 years, numerous new fillers with multi-functional nanocomposites have been developed. Such as for resistance against scratch, transparent coatings in cell phones and compact-disc technology nanoparticle filled amorphous polymers are extensively employed [39].
- To enhance out-of-plane characteristics and to add conductivity and sensing capabilities of traditional composites nanocomposites are used [40]. Micrometer-scale fillers can cause early disaster in material [41], [42] while on the other hand, nanofillers possess reduced magnitude and provide ductility and toughness to nanocomposites which lessen disaster in composite materials [43], [44], cause upsurge in electrical breakdown strength besides impart durability to these composite materials [45].
- Nanoplatelets, nanoparticles, nanotubes (a) and large volume of interfacial polymer (b) is given below [36]

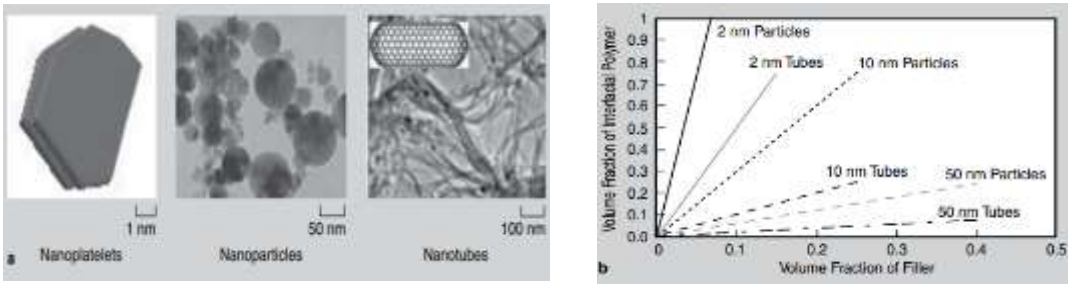


Fig. (a) nanoplatelets (one dimension), nanoparticles (having dimension less than 100 nm), and nanotubes (two dimensions), (b) plot of volume of interfacial polymer centered on interfacial region with thickness of 10 nm surrounding individual nanoparticle and this interfacial region volume has inverse relation with size of nanoparticle (image reprinted with permission) [36].

Fluorescence Spectroscopy

In fluorescence spectroscopy, incorporation is achieved in the form of a fluorescent probe employed at a minimal concentration**.** Probe incorporated into the polymer matrix yield supporting evidence associated with polymer science such as changing aspects of polymer chains via excimer fluorescence [46], phase partition in addition to polymer miscibility, transport methods or polymer deterioration [47].

Zammarano et al. employed Förster resonance energy transfer (FRET) for the purpose to investigate interface and dispersal in polymer nanocomposites. Energy transfer amongst donor (fluorophore in an excited electronic state) to an acceptor one is best defined by FRET mechanism. This energy transfer takes place via nonradiative dipole-dipole coupling. FRET process is highly dependent on distance that is 1 to 10 nm between two molecules. This process is used to study the nanofeatures at border of a polymer–filler system. They studied dispersal of the supporting phase with nanofibrillated cellulose (NFC) fluorescently labelled with 5-(4,6-dichlorotriazinyl) aminofluorescein (FL), acting as acceptor, which is distributed on polyethylene doped with Coumarin 30 (C30), acting as a donor. Use of FRET for interface study in polymer composite is given in

Fig. *3* [48].

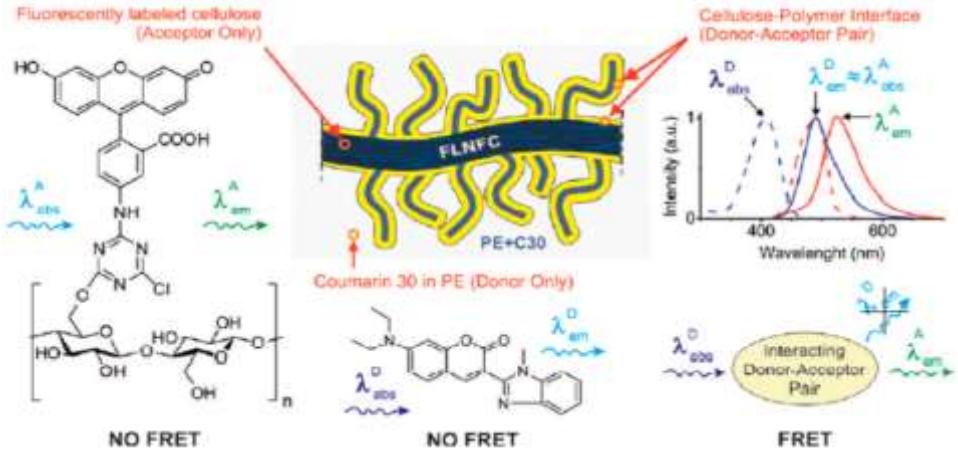


Fig. 3| Graphic representation of use of FRET to study/ reveal interface in polymer composites (image reprinted with permission) [48].

For melt-process polymer clay nanocomposite analysis of intercalation and exfoliation, fluorescence, behavior of optical probes (Nile Blue A besides methylene blue) in polystyrene in addition to polyamide-6 play a vital role [49]. Results of incarceration on glass transition temperature along with physical aging in polystyrene, poly (methyl methacrylate) and poly (2-vinyl pyridine) nanocomposites was studied using fluorescence having 10 to 15 nm diameter silica nanospheres or 47 nm diameter alumina nanospheres [50].

Fluorescence spectroscopy is also helpful in studying stress-softening process in filled elastomers (since filled elastomers have high tensile strength) and this process is known as Mullin's effect. Clough et al. worked on the stress-softening effect and observed that mechano-luminescence on bis (adamantyl)-1,2 dioxetane (mechanophore) hold inside the cross-linker and 9,10-diphenylanthracene (DPA) were contained in silica-filled poly (dimethyl siloxane) break down

mechanophore and forms ketone in excited state which then come to ground state and eliminate light which was taken up by DPA (acting as an acceptor molecule) in this case. Process of this energy transfer is FRET mechanism involving donor and acceptor molecules for energy transfer [51].

Solid-state NMR spectroscopy

Sensitivity of NMR spectra along with relaxation factors to the polymer chains are the basis which form solid-state NMR spectra as suitable spectra for study of polymer-filler interfaces. To distinguish polymer performance in interfacial section from bulk, solid-state NMR spectra was applied. Formulae (transverse magnetization relaxation function) used to find out two dissimilar spin–spin relaxation times, T2, linked to polymer in solid-state proton NMR studies is given below:

$$M\,(t) = M_0 exp\left[\frac{-t}{T_2^{mob}}\right] + (1 - M_0)\, exp\left[\frac{-t}{T_2^{rig}}\right]$$

Where; T_2^{mob} is spin-spin relaxation time linked to polymer in the bulk while T_2^{rig} is spin-spin relaxation time of polymer present at interface and M_0 is portion of mobile chains external to adsorption coating. Formulae employed to find width of interfacial layer is given below:

$$e = R\,[(1 + \frac{\omega(1-\varphi)}{\varphi})^{\frac{1}{3}} - 1]$$

Where: ω is portion of polymer, which is immobilized, ϕ is volume portion of filler while R is radius of particles studied. Dewimille et al. observed thickness of 1.5 nm in his work. In case of tin-catalyzed silica-filled poly (dimethyl siloxane) composites, proton NMR relaxation statistics is given in Fig. *4* [10].

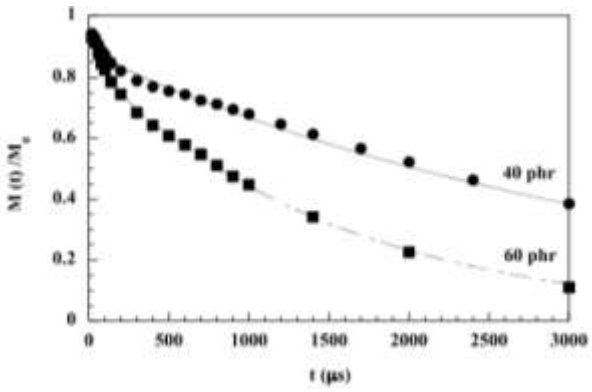
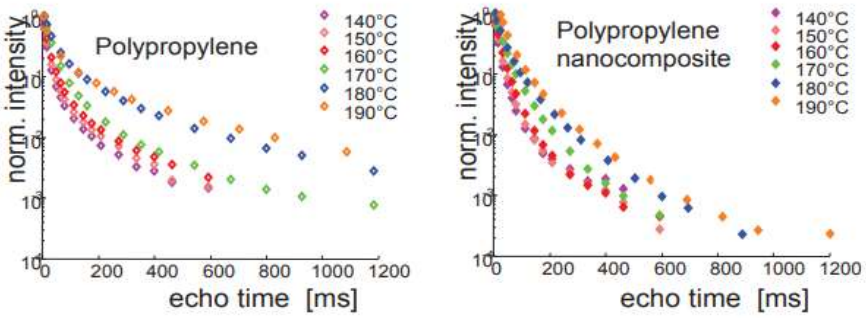


Fig. 4| Tin-catalyzed silica-filled poly (dimethyl siloxane) composites, proton NMR relaxation statistics (image reprinted with permission) [10].

Böhme and Scheler worked on poly (propylene) as well as a poly (propylene nanocomposite) and investigated temperature measurement in melt. Results showed (given in

Fig. *5*) that in both samples (pure and nanocomposite polymer), relaxation period shows the probable two component decay. From results, it was found that in case of pure polymer, longer component has direct relationship with temperature and motion of polymer chains has direct relation with temperature. While in case of nanocomposite, temperature has less influence on chains mobility as compared to unadulterated polymer. The cause of this constrained motion is the interaction of filler with polymer chains leading to restricted motion of polymer chains [52].



(a) **(b)**

Fig. 5| Results of T2 statistics for poly (propylene) (a) and Poly (propylene) nanocomposite (b) as a function of temperature (image reprinted with permission) [52].

Solid state NMR finds applications in characterization of polymers, chemical shift extent, line forms in addition to relaxation time [53]. [54]. Proton–proton double quantum correlation spectroscopy, heteronuclear correlation NMR or solid-state deuterium quadrupolar-echo spectra also used in addition to solid state NMR spectra for the investigation of polymer interface properties [18].

To study poly (ethyl acrylate)/ vycor composite having a 50-microsecond as well as a 50-millisecond spin diffusion delay time, the interface, proton–silicon heteronuclear correlation trials were used. For spin diffusion, 50-microsecond is short and a correlation amongst proton at 4.5 ppm and Q_3 vycor silicon surface sites was observed which is given in Fig. *6* (part a) while Fig. *6* (part b) represent connection amongst polymer protons at 1.3 ppm and 4 ppm besides Q_3 vycor silicon surface sites having spin dispersal delay of 50 millisecond. From this observation, authors make conclusion that central space of the pore is engaged by the polymer and water layer provides insulation to it from silica surface [55].

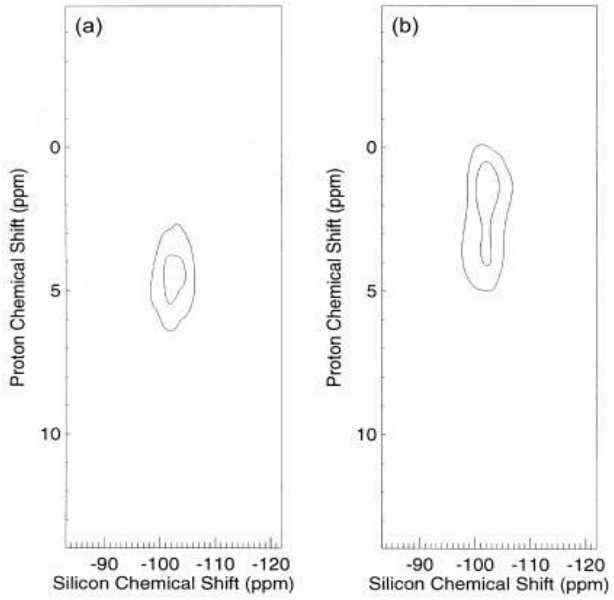


Fig. 6| 2D proton–silicon heteronuclear correlation spectra for the poly (ethyl acrylate)/ vycor composite having (a) 50-microsecond in addition (b)50-millisecond spin diffusion delay time (image reprinted with permission) [55].

For analysis of poly (methyl methacrylate) (PMMA)-based hybrids with modified silica ($mSiO_2$) nanoparticles [56]. Characterization and measurement of relaxation time of SiO_2 and $mSiO_2$ by Si solid-state NMR indicate longer values in the relaxation time of the $mSiO_2 - g - PMMA$ phase in comparison to clear polymer. Additionally, there is an upsurge in the values of T_g of 6 and 12 °C in both nanocomposite of PMMA with neat silica and with modified silica ($mSiO_2$) respectively as compared to PMMA. For the purpose to examine the phase structures along with phase dynamics in both exfoliated and intercalated nanocomposites, variations in molecular motion and relation between two components, solid-state NMR spectroscopic analysis of polymer/ clay nanocomposites was carried out [57], [58].

Infrared and Raman Spectroscopy

Vibrational properties of polymers help to determine the information about polymeric systems using molecular spectroscopies such as Infrared and Raman spectroscopy. When frequency of incident infrared radiations resonates with the specific vibrational mode, then from this kind of resonance interaction infrared radiation spectra occurs (used for thin film study of polymers) and inelastic scattering of light, when a light from a monochromatic source is given to a molecule, resulted in the Raman effect (for investigation of thick films of polymers) [18].

Infrared spectroscopy. Cole studied applicability of the infrared spectroscopy intended for characterization purposes i.e., characterizing state of intercalation as well as exfoliation in polymer nanocomposites made from montmorillonite-founded nano clays. Results showed that form of clay Si-O band envelope amongst 1350 as well as 750 cm^{-1} as a function of processing (which is because of good intercalation and exfoliation). Author also claimed that these results are also due to the fact that when some kind of compatitibilizing agent was added to the clay it resulted in the formation of connections amongst this capitalizing agent as well as Si-O dipoles of nano clay [59].

To characterize state of dispersal of layered silicate in polymer nanocomposite grounded on poly (hexamethylene isophthalamide) (aPa) as well as montmorillonite nanoclay (MMT), Zhang et al. employed Fourier transfer infrared

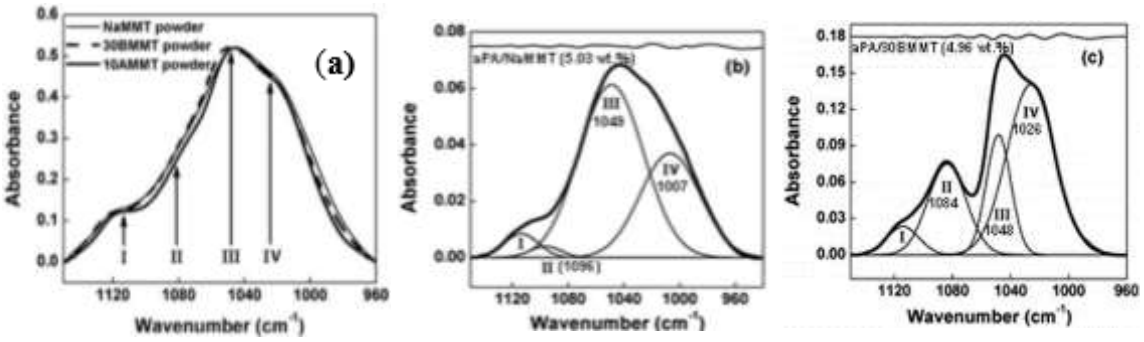


Fig. 7| FTIR spectra of sodium montmorillonite (NaMMT), 30 BMMT, and 10 AMMT powder. Peaks I, II, III, and IV are positioned at 1100, 1082, 1050, and 1030 cm^{-1} correspondingly. (b) FTIR difference spectra of Si-O stretching region for aPA nanocomposites having NaMMT with 5 % clay loading. Maximum peak occurs at 1096, 1049, and 1006.9 cm^{-1}. (c) FTIR difference spectra of Si-O stretching region for aPA nanocomposites having 30BMMT with 5 % clay filling. Maximum peak occurs at 1083.7, 1048, and 1026 cm^{-1}. Position of peaks (i.e., peak II, III and IV) is labelled and curves in each spectrum best describe the difference between actual data and the best fit curve. (Image reproduced with permission).

(FTIR) spectroscopy. The Si-O band envelope of NaMMT (sodium montmorillonite), as well as two organoclays (given in **Error! Reference source not found.** a) shows four usual components. It was also noted that infrared spectra of these both clays and pristine clays are almost like each other which makes it clear that absorption band of agglomerated nanoclay powder does not affect by intercalated organic surfactants. In polymers with unmodified clay particles, the obtained spectral pattern is wider with lesser intensity (shown in **Error! Reference source not found.** b) as compared with delaminated organoclay in same matrix (given in **Error! Reference source not found.** c). Out of plane vibration mode of Si-O bond (shown by peak II) shifts towards lower wavenumbers while in plane vibration mode of Si-O bond (shown by peak IV) shifts toward higher wavenumbers in exfoliated structure. As of this study, it can be concluded that clay dispersal in host polymeric matrix can be indicated with the help of clay Si-O band envelope [60].

Infrared spectroscopy reveals that the surface alteration of carbon nanotubes throughout functionalization procedure has remarkable effect in improving compatibility of carbon material together with polymer matrix [61], [62], [63]. Lee et al. worked on surface modification of carbon nanotube composites using acid, heat, and hydrogen peroxide. First, acid treatment (a two-step mechanism) was carried out. For this purpose, 65 % solution of 3:1 mixture of H_2SO_4/HNO_3 in water was used followed by ultrasonic excitation to the suspension for 1 hour keeping the temperature 80 °C. This acid treatment resulted in attachment of carboxyl as well as hydroxyl groups on the exterior of CNTs. After this, CNTs was washed by distilled water after which filtration and drying occur in vacuum oven at 50 °C for 2 days. In hydrogen peroxide treatment, CNTs were distributed in 1:1 mixture of H_2O_2/ distilled water for introducing hydroxyl as well as carboxyl groups over the exterior of CNTs. After this hydrogen peroxide treatment, washing, filtration and drying of sample was carried out. In third treatment, i.e., heat treatment, heating was done for one hour in a furnace at 500 ℃ with air circulation. Infrared spectrum of H_2O_2 treated CNTs showed strong band at 1089 cm^{-1} which relates to the presence of many C-O bonds on exterior of the CNTs as a result of hydrogen peroxide treatment (resulting in improved stability of poly (amide/ imide)/ CNT composite towards heat) [64].

Deniz et al. worked on poly (vinylpyrrolidone) PVP incorporating with gold nanoparticles and showed from infrared analysis that there were interactions between carbonyl groups of PVP i.e., poly (vinylpyrrolidone) and metal particles [65]. Al-Attabi et al. worked on preparation as well as characterization of polyurethane composites comprising graphene along with gold nanoparticles. FTIR results revealed that there are no strong connections amongst the polymer chains plus merged fragments. Moreover, mechanical properties and tensile strength of modified polyurethane (AuNPs/ graphene/ PU composites) are poor as compared to unmodified polyurethane. This is because of the reason that particle agglomeration creates a lot of imperfections within the composite matrix leading to poor mechanical strength [66].

When Ag nanoparticles were added to Polyaniline/ diamond/ functionalized multi-walled carbon nanotubes (MWCNTs), then their characterization shows a peak on 1036 cm^{-1} which confirms an interactions amongst polyaniline plus silver nanoparticles [67]. Infrared spectroscopy also finds applications in analysis of orientations of polymer chains occurring uniaxially-unfilled as well as filled elastomeric networks. Study of orientation performance of filled networks leads to the assessment of the degree of bonding amongst polymer and filler [68], [69]. Infrared spectroscopy also useful in quantification (by determining the quantity of reactive spots for each nm^2 of filler exterior) of degree of bonding of network layers to filler exterior [70].

Cole et al. find out orientation of equally polymer chains as well as clay platelets in blown films of composites founded on polypropylene along with clay particles using infrared spectroscopy and "the tilted film method". They concluded that clay orientation was relatively high-level owing to high anisometric nature of that kind of filer as compared to those polymer chains having modest level of orientation [71]. However, in work of Bokobza et al. it was found that there was no such great change in extent of molecular orientation of polystyrene (PS) after carbon nanotube addition. The possible reason of this is that orientation of both main chain $(-CH_2-)$ segments and side groups (i.e., benzene ring) of the polystyrene macromolecule hampers throughout the extending of nanocomposite films [72].

AFM-IR technique, used for the purpose to get infrared spectra with nanoscale spatial resolution, has been reported in detail by Dazzi et al. [73]. Limitations of traditional infrared spectroscopy technique are overcome using AFM-IR technique (combination of atomic force microscopy along with infrared spectroscopy). Applications of this technique include polymers, life sciences, photonics, solar cells etc. Marcott et al. describe some applications of AFM-IR technique in the field of polymer composites. These comprised of an isotactic poly (propylene film) in which SiO_2 particles were added, polymer having carbon black particles as well as a carbon-fiber/ epoxy composite material. Information regarding interphase region amongst specific nanomaterial addition along with bulk polymer can be achieved using AFM-IR technique. An illustration of AFM-IR technique is given in Fig. 8 [74].

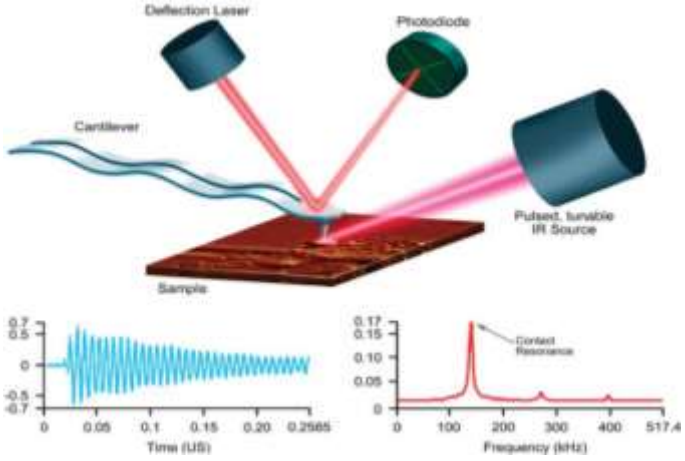


Fig. 8| AFM-IR technique involves the use of pulsed, tunable IR source (for excitation of molecular resonances in trial). Thermal expansion occurs when IR radiations are absorbed leading to excitation of resonant oscillations of cantilever. Cantilever oscillations decline in characteristic ringdowns (underneath left-hand). Fourier techniques were used to analyze these ringdowns for the purpose to bring out their amplitude as well as frequency (underneath right-hand). Contact resonance peak frequencies of cantilever ringdowns determine mechanical toughness of sample (image reprinted with permission).

Raman spectroscopy. With the advent of carbon nanotubes in previous two decades, use of Raman spectroscopy for analysis of carbon-based composites revived [75]. This technique widely used for characterization of vibrational states of wide-ranging range of carbon-centered materials like graphene, graphite, diamond, along with carbon nanotubes etc. Raman spectroscopy is one of the best significant practices meant for study of carbon-centered composites for reason that these composites create solid, well defined bands even at their low concentration owing to resonance-enhanced Raman scattering effects [76]. However, some factors such as strain, pressure, filler-filler as well as polymer-filler interactions, orientation, temperature, plus functionalization etc. disturb spectral features of carbon materials [77].

Laser-induced sample heating shifts vibrational Raman modes of carbon-based materials and are suggested by Everall et al. for use in order to interpret precise Raman data [78]. Laser heating effects of the sample cause an upsurge in the confined temperature shifting the Raman bands towards lower wavenumbers equally for pristine carbon materials as well as for carbon species implanted in polymeric medium. Shift has direct relation with laser power, however, as detected in numerous cases for carbon materials in polymer matrix shift is lower as matched with non-embedded state [78], [77], [79], [80].

By comparing the dispersive behaviour of carbon materials in pure form plus inserted in the matrix, analysis of polymer-filler interface was carried out. Raman spectroscopy has a feature of shifting D as well as G' bands to higher frequencies along with the upsurge in laser excitation energy. For D band, upshift occurs at $50\ cm^{-1}$/ eV and for G' band its value is $100\ cm^{-1}$/ eV. Electronic properties of carbon materials and the excitation-energy reliance of D as well as G' bands remain greatly concerned by interfacial connections amongst polymer as well as filler. That method has been reviewed previously [76], [81], [82] while Srivastava et al. reported contradicted results in their findings [83].

Dispersive behaviour of MWCNTs implanted in polydimethylsiloxane (PDMS) is higher as compared to its pure state. It has also been observed that there exist strong CH-π connections amongst methyl group of PDMS as well as π-electron

rich exterior of carbon nanotube. Modeling studies revealed that a wrapping process around the nanotube exterior takes place owing to extreme elasticity of PDMS chain [84]. CH-π bonding successfully explain the adsorption characteristics of PDMS chains on the CNT exterior which confirms the presence of electrical and mechanical properties in PDMS/ CNT composites [85], [84], [86].

To overcome the drawbacks of conventional Raman spectroscopy tip-enhanced Raman spectroscopy (TERS) i.e., grouping of both Raman spectroscopy plus scanning probe microscopy has been used to obtain nanoscale spatial resolution. In this technique, sharpened metal tip is fixated on base of the laser beam as well as can be placed accurately at various areas on sample exterior. Localized surface plasmon (LSP) resonance and antenna effects on tip apex amongst tip-LSPs as well as laser photons improve besides limit electromagnetic (EM) field causing an increase in Raman signal from analyte particles in surrounding area of tip-apex. Further details about advances and technology of TERS can be found in the literature [87], [88]. Schematic diagram of tip-enhanced Raman spectroscopy is shown in Fig. 9 and Fig. 10.

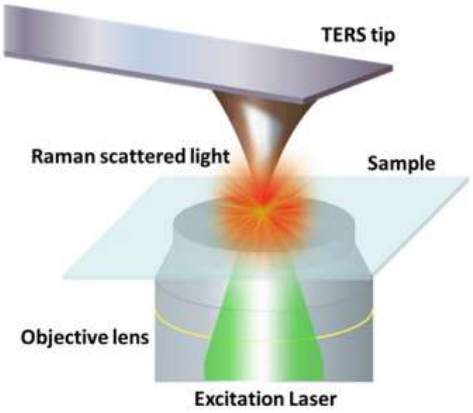


Fig. 9| Schematic diagram of tip-enhanced Raman spectroscopy showing principle of atomic force microscope (AFM)-centered tip-enhanced Raman spectroscopy (TERS) in transmission manner. Localized surface plasmon (LSP) resonance on tip apex amongst tip-LSPs as well as laser photons improves besides limits electromagnetic (EM) field causing an increase in Raman signal from analyte particles in surrounding area of tip-apex (image reprinted with permission) [87].

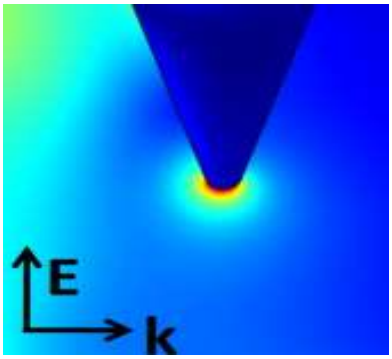


Fig. 10| Incidence of p-polarized laser having electric field (E) parallel to tip-axis on metal resulting in improving EM field intensity to improve besides limits at tip-apex [87].

Saito and Yanagi worked on β-carotene condensed in single-walled carbon nanotubes (SWCNTs) and analyzed TERS spectra in 100 nm steps all along single tube bundles corresponding to each other. Frequency of encapsulation of β-carotene was not consistent (indicated by lack of β-carotene in certain spectra). This shows the superiority of TERS on the way to prevent averaging of Raman spectra for spatially non-uniform nanocomposite materials [89]. Yano et al. studied nanoscale uniaxial pressure effect on single-walled carbon nanotubes using TERS with tip pressure causing shift in peak position as well as alteration in Raman strength (which indicate tube deformation) [90]. Yano et al. showed that nanoimaging using TERS technique can disclose strain distribution alongside the length of isolated carbon nanotubes [91].

Vantasin et al. explained the applications of TERS for study of structure as well as connections of different types of carbon and graphene-centered nanomaterials [92]. Suzuki et al. employed TERS to investigate local connections at boundary of styrene-butadiene rubber (SBR)/ multiwalled carbon nanotube composites (MWCNTs). TERS bands are

strong owing to SBR phenyl parts (at strong MWCNT bands) while bands owing to vinyl parts are strong only as soon as MWCNTs are weak. Results indicate that alteration in orientation of phenyl rings with π-π interactions amongst polymer chains as well as MWCNTs is responsible for modification in local distribution of polymer chains [93].

Polymer-metal nanocomposites are used in the same way as surface-enhanced Raman scattering (SERS) substrates [94], [95], [96], [97]. SERS is defined as molecular spectroscopic technique which increases Raman intensity of molecules adsorbed on irregular metal exterior specially of silver or gold [98]. Graphene also finds extensive applications in surface-enhanced Raman scattering (SERS). Some aromatic molecules when adsorbed on the exterior of graphene sheet, it causes an upsurge in Raman signal of adsorbed molecules. This upsurge in Raman signal is an indication of strong connections amongst substrate as well as molecules which helps in charge shifting [99]. Metal nanoparticles combined with graphene on the way to build a graphene-mediated surface-enhanced Raman scattering [100].

Conclusions

For the purpose to study the characteristic properties, characterize and development of new materials using polymer nanocomposites, several molecular characterization techniques are available and are in use today. This review article briefly summarizes the knowledge in the current characterization techniques and study the applications of fluorescence, solid-state nuclear magnetic resonance (NMR), infrared, plus Raman molecular characterization techniques for characterization of polymers, filler, and composites. Fluorescence study (for studying/ analysis of exfoliation or intercalation in clay composites), unlike infrared and Raman is not sufficient for detailed analysis of molecular structure. Solid-state NMR is an effective technique (which carry out analysis via determination of relaxation time) for study of region at polymer-filler interface. Infrared spectroscopy, on the other side, is used for material characterization via bands/ peaks specific for each functional group of the polymer. Above all, Raman spectroscopy is significant technique meant for chemical analysis of carbon-founded materials which will produce resonance-enhanced scattering effects even at their very small amount in the composite materials.

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Author's contribution

All authors contributed equally to manuscript.

Conflicts of interests

Authors state no competing financial concerns to influence the work described in this research.

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