



LASER RAMAN STUDIES OF FIBROUS POLYMER - A REVIEW

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This review covers the development of understanding of polymer morphology of fibrous polymers using Raman Spectroscopy. Morphology refers to form and structure that a polymer exhibit and is influenced by the local microstructure of the back-bone chain. In chain like polymer molecules, the vibration of the carbon chain is easily studied by using Raman spectroscopy. The utility of this technique in characterization of polymer morphology, identification of phase composition and determining changes in orientation in drawn polymeric materials is presented. Work carried out on fibrous structures that are subjected to uniform stress or strain and their responses as monitored by laser Raman have been documented. Nondestructive techniques like Raman Spectroscopy are required for the identification of materials in many applications such as in forensic science, quality assurance and fabric defects analysis on the basis of morphology of individual components. Outcome drawn from the analysis of applications from these fields are presented in this paper.

KEYWORDS: Raman Spectroscopy, Polymer Morphology, Degradation, Orientation.**INTRODUCTION**

Analysis of polymer morphology has been an important aspect of basic research as well as applied applications like forensic science and industrial quality assurance. Basic research focuses on morphological parameters. Morphology refers to form and structure that a polymer exhibit and is strongly influenced by the local microstructure of the back-bone chain. These structural characteristics influence the mechanical and other functional properties that distinguish them. Various instrumental techniques are required to identify and study the polymer morphology. Among these Raman spectroscopy has emerged as a unique tool for the characterization of polymers, identification of phase composition, and determining orientation changes in drawn polymeric materials and online monitoring of industrial processes [1-5]. Raman spectroscopy is convenient and informative in determining the primary and secondary structure of polymers. Raman spectroscopy has great utility in the characterization of polymeric fibers because of low fluorescence background and the ability to obtain both second and fourth-order orientation function from polarized data [6]. The portability of the technique allows for its use in on-line process monitoring of effect of firing temperature and polymer drawn during manufacturing. [Cis/Trans] ratios in polymeric composites have been studied as a function of temperature [7, 8]. Polyethylene production has been monitored for amorphous phase orientation and deformation in uniaxially drawn material [9, 10]. Raman Spectroscopy has also been utilized to study the extent of stress during the manufacture of composite leading to design improvement [11]. Raman Spectroscopy is believed not only convenient and informative but also a powerful

analytical tool with some particular advantages for the analysis of polymers. During the last 25 years, this technique has emerged as an indispensable instrument for the study of materials. Some excellent studies and reviews [4, 5, 11-15] have been documented in the literature for delineating structural details such as, Chemical structure and Composition, Stereo order, Conformation order, Physical arrangement of polymer chains both in the solid and in the melt, crystalline, Mesomorphous and Amorphous phases, Lamellar thicknesses, Orientation and side group alignment in anisotropic polymers, Surface and Interface structure, Degradation and Stress sensing in Nanocomposites of polymeric materials.

BASIC CONSIDERATIONS**(A) Raman Spectroscopy**

Raman spectroscopy is a form of molecular spectroscopy that involves the scattering of impinging electromagnetic radiation by the cloud of electrons round the nuclei or by the molecules in the sample to form a short-lived state called a 'virtual state'. Such states are formed through the polarizability of molecules. Polarizability is related to the ability of electronic clouds surrounding the molecule to interact with an electric field associated with it. Raman spectroscopy probes the vibrational, rotational and other low frequency modes of molecules and is recorded as inelastically scattered light. This state is not stable and subsequently the photons are quickly re-radiated. If only electron cloud distortion is involved in scattering, the photons will be scattered with very small frequency changes. This scattering process is regarded as elastic scattering and is the dominant process. For molecules it is called Rayleigh scattering. However, if nuclear motion is induced during the scattering process, energy will be

transferred either from the incident photon to the molecule or from the molecule to the scattered photon. In these cases the process is inelastic and the energy of the scattered photon is different from that of the incident photon by one vibrational unit.

In the case of long polymer chains, vibrations of their backbone usually do not generate changes in the moment because their repeating units negate adjacent dipoles. However, they demonstrate drastic changes in polarizability. For this reason, Raman spectroscopy is especially suitable to study structural changes and conformation of the polymer backbone. The Raman spectra provide the following information. 1. The wave number position in the spectra indicates the composition (vibrational states) of the sample being examined. 2. The change in the width of characteristic peaks describes the molecular structure (amount of plastic deformation, changes in crystallinity, etc.). 3. Intensity of peaks denotes the amount of material or the number of scattering units in a given volume. 4. A shift in frequency of characteristic Raman peaks can indicate mechanically strained structure [1-6].

In practice, modern Raman spectroscopy is simple. Variable instrument parameters are few, spectral manipulation is minimal and a simple interpretation of the data may be sufficient to draw important information. It is known that Raman scattering is inherently a weak process in that only one in every 10^6 – 10^8 photons that gets scattered is available for analysis. This is true in the case of low scattering specimens. However the discovery of surface-enhanced Raman scattering (SERS), has overcome this limitation to an extent. SERS refers to the phenomenon that the Raman signal from adsorbates on roughened metal surfaces is enhanced by a factor of 10^4 – 10^6 due to the excitation of surface Plasmon resonance on roughened metals [16].

(B) Comparison of Raman and IR spectroscopy

When light interacts with matter, the photons which make up the light may be absorbed or scattered, or may not interact with the material and may pass straight through it. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state. It is this change which is measured in absorption spectroscopy by the detection of the loss of that energy of radiation from the light. However, it is also possible for the photon to interact with the molecule and get scattered.

The way in which radiation is employed in infrared and Raman spectroscopy is different. In infrared spectroscopy, infrared energy covering a range of frequencies is directed onto the sample. Absorption occurs where the frequency of the incident radiation matches that of a vibration so that the molecule is promoted to a vibrational excited state. The loss of this frequency of radiation from the beam after it passes through the sample is then detected. The IR spectroscopy determines vibrations that cause a change in the dipole moment of a molecule. In contrast, Raman spectroscopy uses a single frequency of radiation to irradiate the sample and it is the radiation scattered from the molecule, one vibrational unit of energy different from the incident beam, which is detected. Raman spectroscopy

determines vibrations that cause a change in the polarizability of a molecule. Thus, unlike infrared absorption, Raman scattering does not require matching of the incident radiation to the energy difference between the ground and excited states.

However, there are some vibrations that induce changes in both polarizability and dipole moment. These vibrations can be determined through the use of both IR and Raman spectroscopy. IR spectroscopy is suitable for side chain analysis, thus enabling both techniques to be complementarily in deriving structural information [6].

(Fig 1) shows the information derived through Raman and IR spectra of the same polyethylene (PE) [5]. As is known, if the polymer molecule is symmetrical, it generates greater difference between Raman and IR spectra. The PE molecule has a center of symmetry, and the Raman and IR spectra exhibited entirely different vibrational modes. In the Raman spectrum, the C-C modes are dominant whereas CH_2 modes in IR spectra are more visible.

(C) Polymer structure

Macroscopic properties of materials are closely related to their microstructure. Normally polymer materials with desirable mechanical properties are produced by means of drawing at temperatures close to the temperature of melting. Maximum orientation of macromolecules with respect to the direction of drawing can be achieved leading to the production of high modulus fibers and films. Such polymeric materials have a complex heterogeneous structure, featuring crystalline and non-crystalline areas altering along the orientation axis. This orientation function usually differs for macromolecules in crystalline and non-crystalline region. For semi crystalline polymers, the ratio of crystalline and amorphous phases and molecular orientation in these phases are considered to be essential functions to understand the relationship and to optimize physical properties of the material. Polymer molecules in such systems are invariably twisted, folded, bent, intertwined and associated with one another. There are always multi-component mixtures of molecules of varying molecular weight, degree of branching and chain end groups. Presence of oxidative impurities or residual impurities from the synthesis of the polymer adds to the polymer structure complexity [17].

STUDY OF POLYMERIC MATERIALS BY RAMAN SPECTROSCOPY

Nondestructive techniques like Raman Spectroscopy are required for the identification of materials in many applications like the identification of materials, forensic science, quality assurance and fabric defects analysis on the basis of morphology of individual components.

Li-Ling Cho and Carrilo et al [18, 19] applied Raman Spectroscopy to identify and differentiate of similar structured fibers. Li-Ling Cho [18] differentiated Cellulosics, Wool and silk and synthetic fibers like nylons and acrylics. Viscous rayon was differentiated with cotton by the presence of an extra Raman response at 650 cm^{-1} , indicative of incomplete Xanthane derivative in the regenerated viscous fiber (Fig 2a). Wool and silk are protein fibers with similar structure. However wool could be differentiated due to the presence of an amino acid, Cystine band which appeared at 523 cm^{-1} (Fig 2b). Acrylic

consists of various types of fibers based on the percentage of Polyacrylonitrile in them. Modacrylic fiber contains between 35 to 85% Polyacrylonitrile, whereas acrylic fiber contains more than 85 % Polyacrylonitrile. (Fig 3a) shows a Raman spectra of acrylic fibers made from PAN and Methylmethacrylate(MMA). (Fig 3b) shows Raman spectra of modacrylic fiber made from Polyaniline (PAN) and Vinylidene Chloride. Acrylics can be specifically identified by nitrile band at 2254 cm^{-1} . However Modacrylic can be differentiated from acrylic by the additional band at 465 cm^{-1} . Raman spectroscopy has been utilized to differentiate three types of Nylon namely N-6, N 6-6, and N 6-12. Nylon 6 has a characteristic Raman peak at 1281 cm^{-1} . Subtle difference in the C-C backbone at 1126 cm^{-1} and 1062 cm^{-1} showed two peaks for Nylon 6, but three peaks for Nylon 6-6 and nylon 6-12. The peak at 1235 cm^{-1} (N-H Wagging) is absent for Nylon 6-12. Thus author demonstrated that structurally similar nylons can be differentiated by the Raman Spectroscopy (fig 4) [18].

Raman spectroscopy facilitates examining the orientational changes during drawing of polymers. During extrusion polymers are oriented to impart mechanical properties. In the case of uniaxial stretching of PE, the elastic modulus rapidly increases with the extent of group orientation [8, 20]

Prokhorov et al [12] investigated the evolution of the Raman spectrum of PE within the C-H stretching region in the process of uniaxial deformation and emphasized that the peaks at 2848 and 2882 cm^{-1} are due to dominant orientational changes [12]. The intensity of scattering rapidly decreased with the growth to draw ratio at various regions in a PE bottle. Reduction in the intensity was strongest in the neck region. (Fig 5) shows marked reduction of Raman peaks at 2882 and 2848 cm^{-1} as the draw ratio increased.

Marie Pigeon et al [8] investigated molecular orientation of PE with respect to stretching. However the emphasis had been to quantify orientation changes in bands located at 1080 , 1130 and 1170 cm^{-1} and up to 1500 cm^{-1} . The result obtained from the 1080 cm^{-1} band showed that the orientation of gauche structure does not vary much with the draw ratio between 7.0 and 11.7. However the 1130 cm^{-1} band indicated that trans conformer in the amorphous phase oriented more rapidly in the draw direction. The authors showed that Raman spectroscopy can provide quantitative information about the molecular orientation of Polyethylene. Tanaka and Young [21] reviewed studies on molecular orientation distributions in poly (ethylene terephthalate) (PET) fibers using polarized Raman Spectroscopy. (Fig 6) represents changes in the Raman spectra of PET fiber with reference to draw ratio. As the draw ratio increases band sharpness improves an indicative of crystallinity development [21].

Raman spectroscopy was used to study variation in the orientational order of macromolecules in the uniaxially drawn intercalated Nanocomposites based on PE, isotactic PP and modified clay. The authors found that for the drawn Nanocomposites, the filler impeded the orientation along the draw direction for the macromolecules localized in the noncrystalline phase of the polymer matrix. However the overall orientational ability of the PE and PP crystallites Nanocomposites was not affected by the fillers

[22]. Raman spectroscopy has been employed for the detection of defects in polymeric systems. Mitra et al. discovered that when conjugated polydiacetylene single crystal fibers were deformed in tension, Raman bands located at 1498 cm^{-1} (corresponding to the -C=C- backbone moiety) and 2104 cm^{-1} (corresponding to the carbon-carbon triple bond backbone moiety) shifted the position towards a lower wave number [23].

Significant morphological breakthroughs were derived from Raman studies on polymers deformed under tension. Raman shifts were observed in high performance poly [P-Phenylene benzobis thiazole(PBT)], high modulus polyethylene and conjugated polydiacetylene single fiber [23-26]. The sensitivity of Raman spectroscopy was brought out not only by the changes in C-C asymmetric stretch mode but by the asymmetric broadening due to 'taut-tie' molecules within the amorphous regions of the fibers as well.

Perhaps the most important contribution to understand the deformation of polymeric fibers using Raman spectroscopy was from a series of papers on rigid-rod fibers; [24, 27, and 28]. The authors showed that for a range of different fibers (Kevlar, Twaron, Technora, PBO, and PET) the stress-induced Raman band shifted for the 1610 cm^{-1} peak, corresponding to the aromatic ring stretch[24, 27, 28]. The symmetrical broadening of 1610 cm^{-1} peak was reported for Kevlar, Twaron, Technora and PBO fibers, whereas PET showed asymmetric broadening. This difference was reported to be due to the fact that some of the bonds in PET must be overstressed, as had been detailed previously [29].

STUDIES ON POLYMER DEGRADATION

Chauhan et al [30] presented Raman studies on photo induced changes in polyolefin and polyolefin-nanoclay films. The studies revealed reduction in the scattering of bands due to imposed strain in C-C bands by solar radiations in amorphous regions in both type of films. The peaks at 1062 cm^{-1} (asymmetric C-C stretching in crystalline) and at 1080 cm^{-1} (C-C stretching mode in amorphous region) showed reduced intensity. Likewise the peak at 1295 cm^{-1} also registered lower intensity after exposure to solar radiations (Fig 7a, 7b). The decrease in intensity has been attributed to the imposed strain in C-C bands. The intensity of a Raman band is also governed by the change in polarisability as a result of incident energy. The solar exposed films indicate change in polarisability as revealed by the Raman spectra of the films. Oxidation of semi crystalline polymers such as polyolefin's having high chain mobility in environmental conditions is generally considered to occur predominantly in the amorphous region, which can be treated as a boundary phase of the neighboring crystalline regions. Thus one of the manifestations of photo oxidation would be a decrease in the Raman sensitive bands and increase in carbonyl group bands.

Raman spectra of non-polar and polar polymer presented interesting features. The nonpolar polymer (PE) revealed reduced scattering, whereas polar polymer namely PET showed increased intensity for aromatic moiety as a result of solar exposure. Studies by Preeti Yadav [31] on PET films of different thicknesses (Fig 8a, 8b) showed

increased intensity for aromatic ring whereas scattering from C-C bonds became lesser intense after exposure to solar and UV radiations. There is an inverse relationship existed between the intensity at 1300 cm^{-1} and $-\text{CH}_2$ -chain length. These films exhibited a direct relationship between exposure duration and degradation of mechanical properties [32]. Janssen et al. [33] reported have studies on degradation of PET films coated on to a steel sheet, with reference to Raman vibrational band at $1096, 1120\text{ cm}^{-1}$, carbonyl band at $\sim 1725\text{ cm}^{-1}$ and confocal depth profile of corrosion products. Use of Raman Spectroscopy to study degradation of polyvinylchloride as well as the structure of polyethylene sulphide has also been reported [34, 35].

In a very involved and interesting study, it has reported that Raman spectroscopy has the potential to study the durability of conservation treatments by probing chemical changes as a result of polymer photo degradation and in studying temporal chemical changes in the fields of archaeology and art history [36, 37]. Authors found Raman spectroscopy more useful in their endeavor, than the other instrumental techniques they employed [37]. Raman spectroscopy has been shown to have some limitations in the assessment of the chemical modifications which occurred during the ageing process. Nevertheless, it remains an efficient technique in the identification of the main components of polyurethane. It has also been demonstrated that the use of photo bleaching and improving the sample preparation are preponderant for enhancing the quality and the reliability of Raman spectra. Raman Spectra of degraded Polyaniline (PANI) films showed shift in band positions as well as reduction in intensity of certain bands and appearance of new bands [38]. The crystallinity of coatings, the degree of molecular order, orientation and cross-linking are measurable by the stereo selectivity of the Raman spectroscopy. This was applied for the classification of PET coatings as well as for the local identification of corrosion products by monitoring the corrosion under transparent organic corrosion protection layers.[39]

MONITORING OF STRUCTURAL CHANGES DURING CHEMICAL REACTION

For many years Raman spectroscopy has been used successfully to characterize polymer materials within the analytical laboratory. Its capabilities for monitoring industrial polymerization processes are now being widely explored as an alternative to more traditional monitoring methods. Demanding applications such as extrusion processes are an example where Raman provides a direct insight into properties such as crystallization and orientation within polymer fibers and films. Raman is also particularly well suited to the monitoring of the polymerization process itself. It is extremely sensitive to the changes in the polymer C=C backbone seen during the conversion of a monomer upon polymerization. Cross linking, curing and other such processes can also be studied in-situ and with greater ease than ever before. Raman spectroscopy has also been utilized to monitor polymerization. Changes in Raman intensities as a function of temperature and time of reaction may contribute to the elucidation of reaction mechanism and kinetics. Raman structural study of reactor blends of

ultrahigh molecular weight polyethylene (UHMW PE) and random ethylene/1-hexene copolymers has been documented for the first time [40]. Raman Spectroscopy has been used to study isomerization process for the conversion of all-*cis* isomer to all-*trans* isomer for the preparation of electroactive polymers [41-43].

Miruna Dorobantu Bodoc et al [44] have reported online monitoring of Vinyl Chloride polymerization using Raman spectroscopy. The Raman band specific to the vinylic group exhibited a strong signal at 1606 cm^{-1} . The low frequency band at 395 cm^{-1} was attributed to the planar deformation mode of the C=C-Cl skeleton, the 707 cm^{-1} corresponds to the stretching of the C-Cl bond, the responses in the $1200\text{-}1400\text{ cm}^{-1}$ area indicated the CH_2 planar deformation or rocking modes and the magnitudes in the $3000\text{-}3100$ area were assigned to stretching modes of the C-H bonds. During polymerization, monomer content decreased with conversion. Therefore the corresponding vinylic C=C related peak area underwent an important decrease according to time [45]. The polymerization rate for acrylamide and methylenebisacrylamide was determined by monitoring the changes in the characteristic vibrational peaks at 1284 cm^{-1} and 1607 cm^{-1} corresponding to the bending mode of CH bond and CC double bonds of acrylamide and in the characteristic peak at 1629 cm^{-1} corresponding to carbon-carbon double bond of methylene-bis-acrylamide using Raman spectroscopy [46].

Structural changes affected by sea water hydrolysis in polyamide fibers have been studied [47]. The Raman spectra of a 1% solution in seawater of a commercially available polyamide were obtained in a sealed glass tube at 120°C for periods of 0, 7 and 90 days, respectively(Fig 9). The amide band at 870 cm^{-1} decrease in intensity with time and after 90 days has disappeared completely. A new band at 920 cm^{-1} , due to the ammonium salt formed as a result of hydrolysis, appears and gradually increases until, after 90 days, hydrolysis is complete. By monitoring the relative intensity changes of these two bands, hydrolysis of polyamide was followed over very long periods, often up to 18 months.

CONCLUSION

The development of synthetic fibers for a variety of applications has invigorated research into the understanding of molecular and crystalline orientations, morphology and deformation. Raman spectroscopy has gained an important place as an analytical tool capable of discerning subtle structural variations affected by the back-bone chain during the formation of polymer structure, changes due to uniaxial drawing as well as assessment of imposed stresses on fibrous polymers and molecular deformations. The effect of crystal orientation has also been reviewed as this plays a critical role in the mechanical properties of synthetic fibers. Moreover the location of the amorphous material in relation to the crystals as a result of environmental changes is presented. Laser Raman has been useful in elucidating effects of photo degradation, photo bleaching and other environmental effects on polymeric materials.

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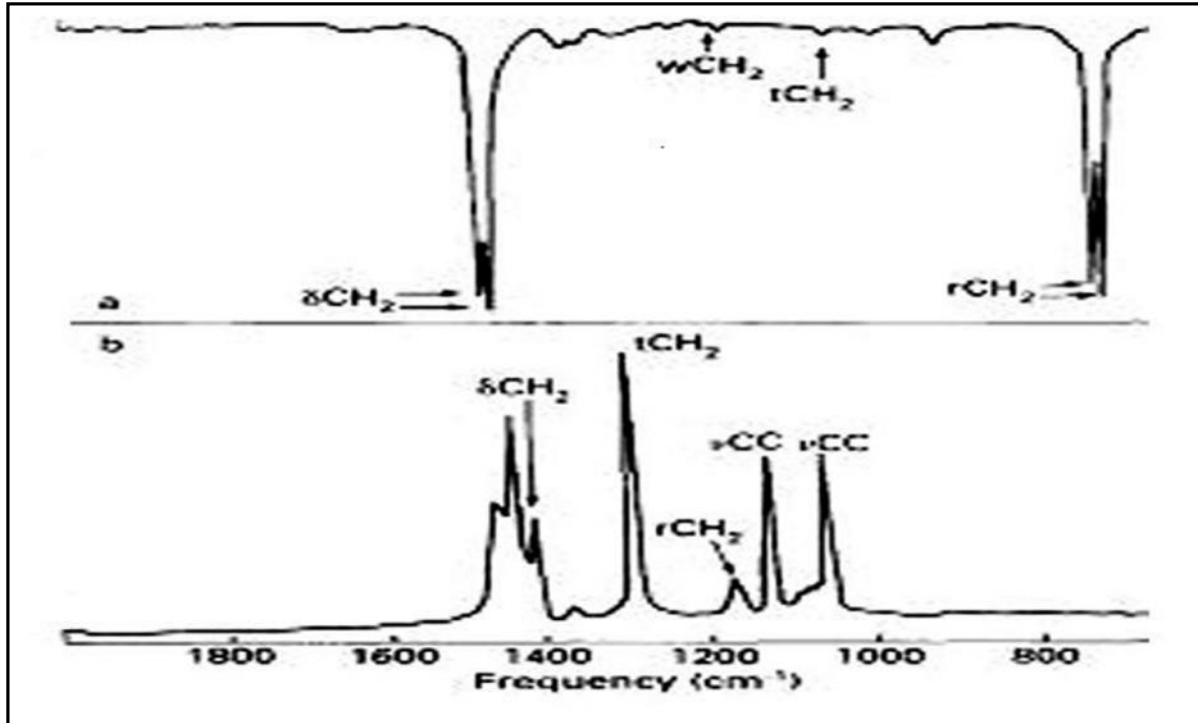


Fig 1: (a) IR Spectra and (b) Raman Spectra of linear polyethylene. [5]

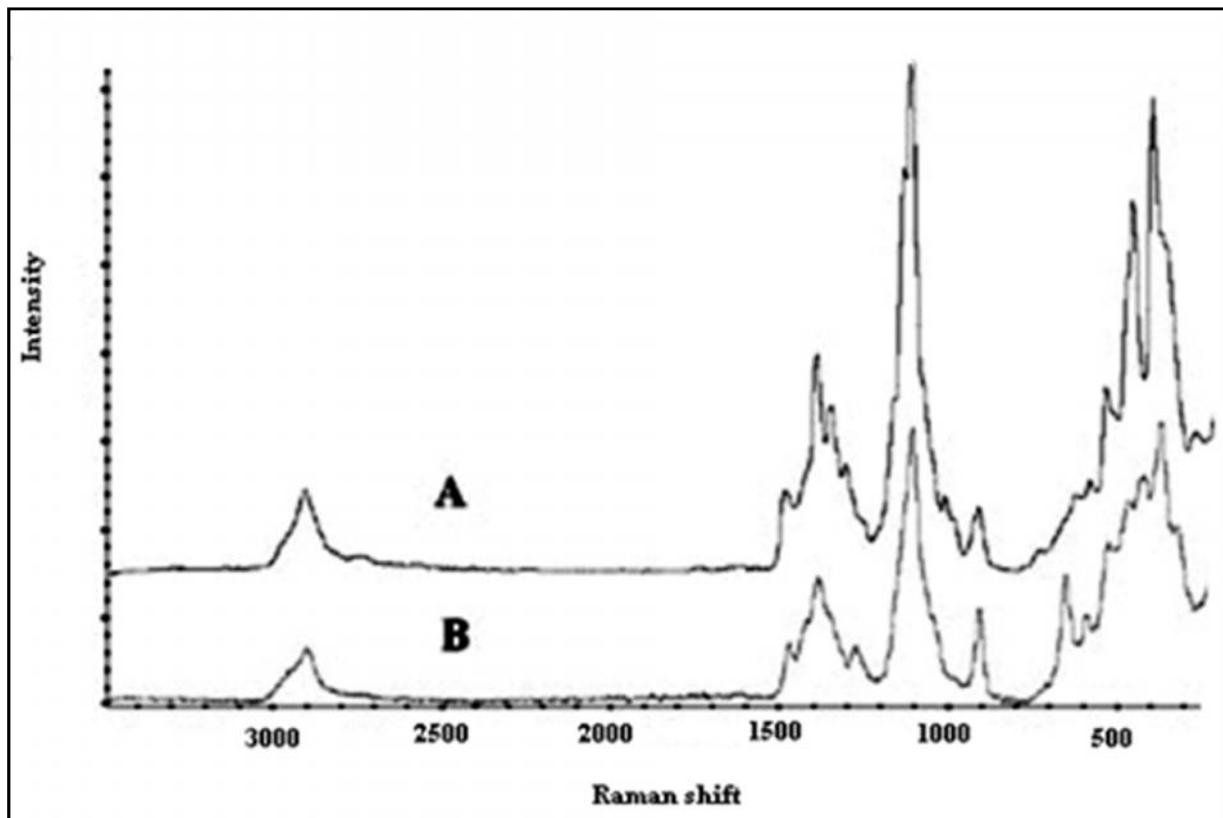


Fig 2(a): Comparison of Raman spectra of two cellulosic fibers; (A) Cotton (B) Rayon. [18]

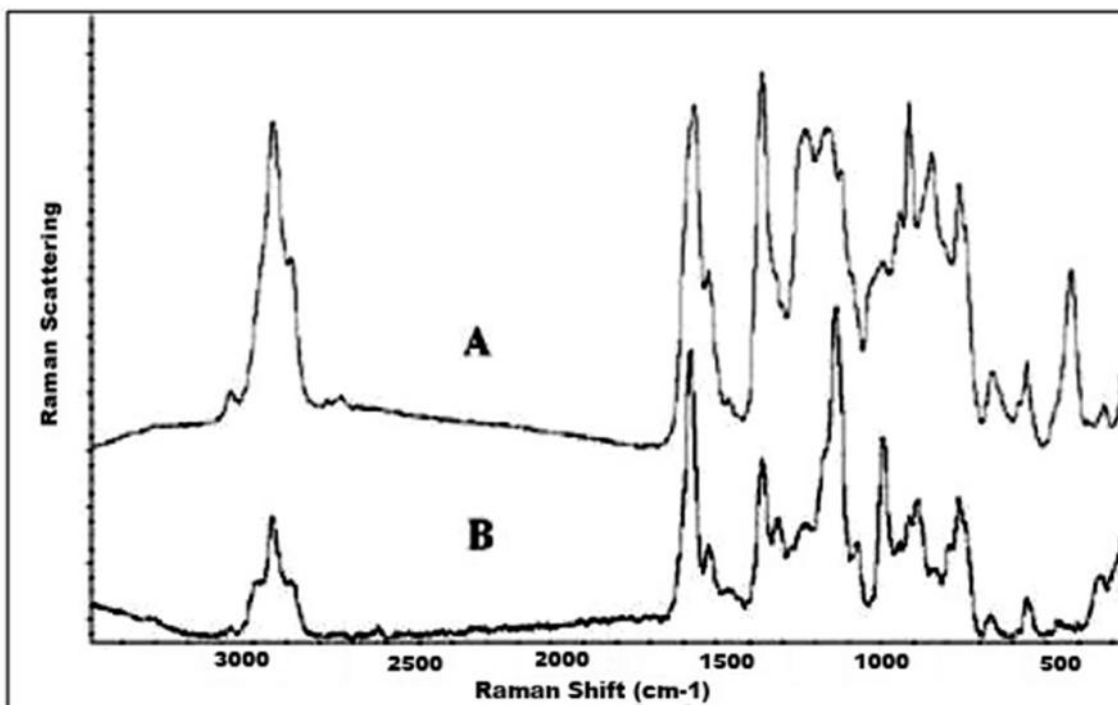


Fig 2(b): Comparison of Raman Spectra of two animal fibers (A) Wool (B) Silk. [18]

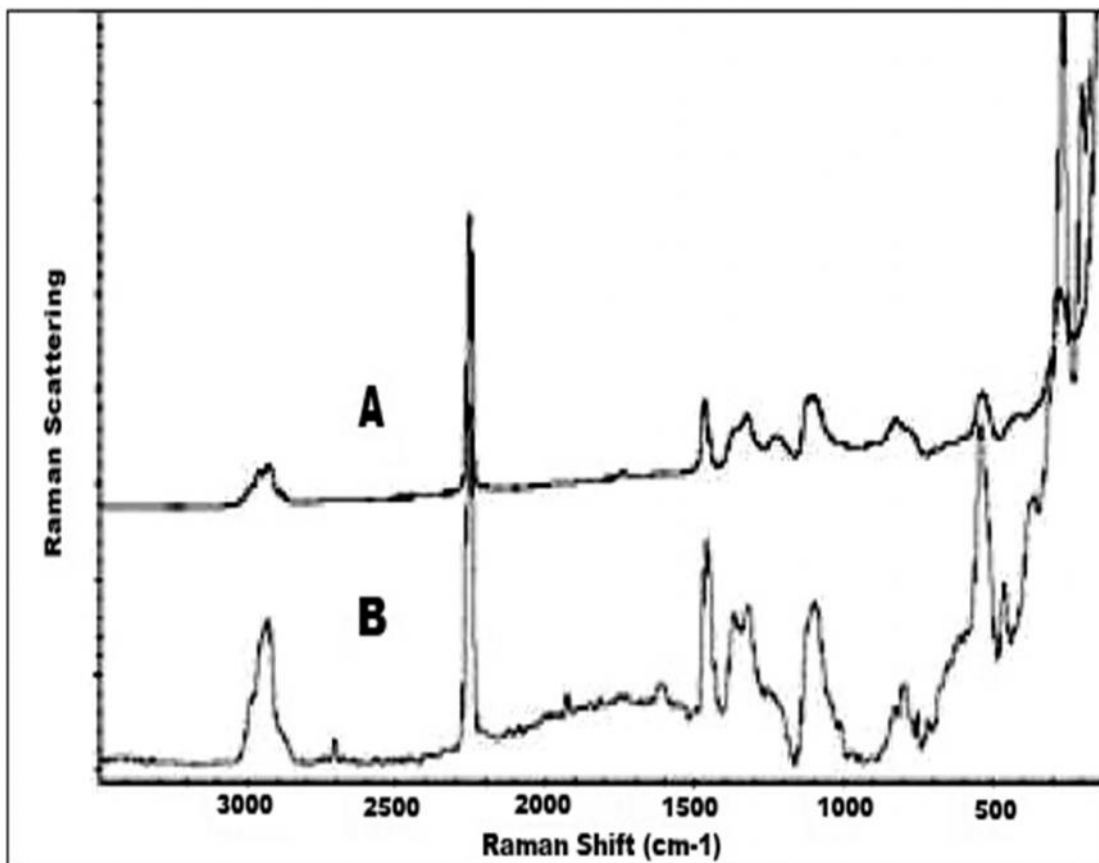


Fig 3: Raman spectral results of (A) Creslan 61 Acrylic (B) Modacrylic fiber. [18]

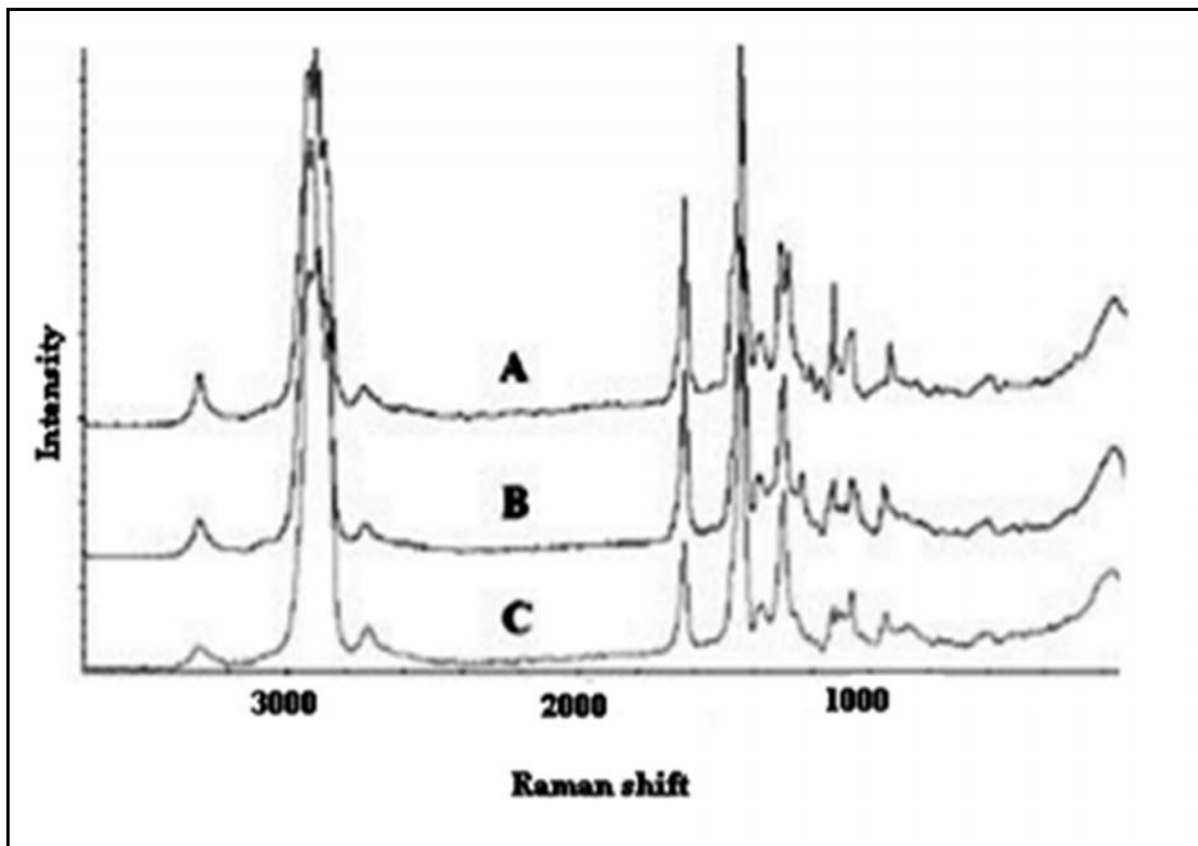


Fig 4: Raman spectral results of nylon fibers nylon 6 (B) nylon 6- 6 (C) nylon 6- 12. [18]

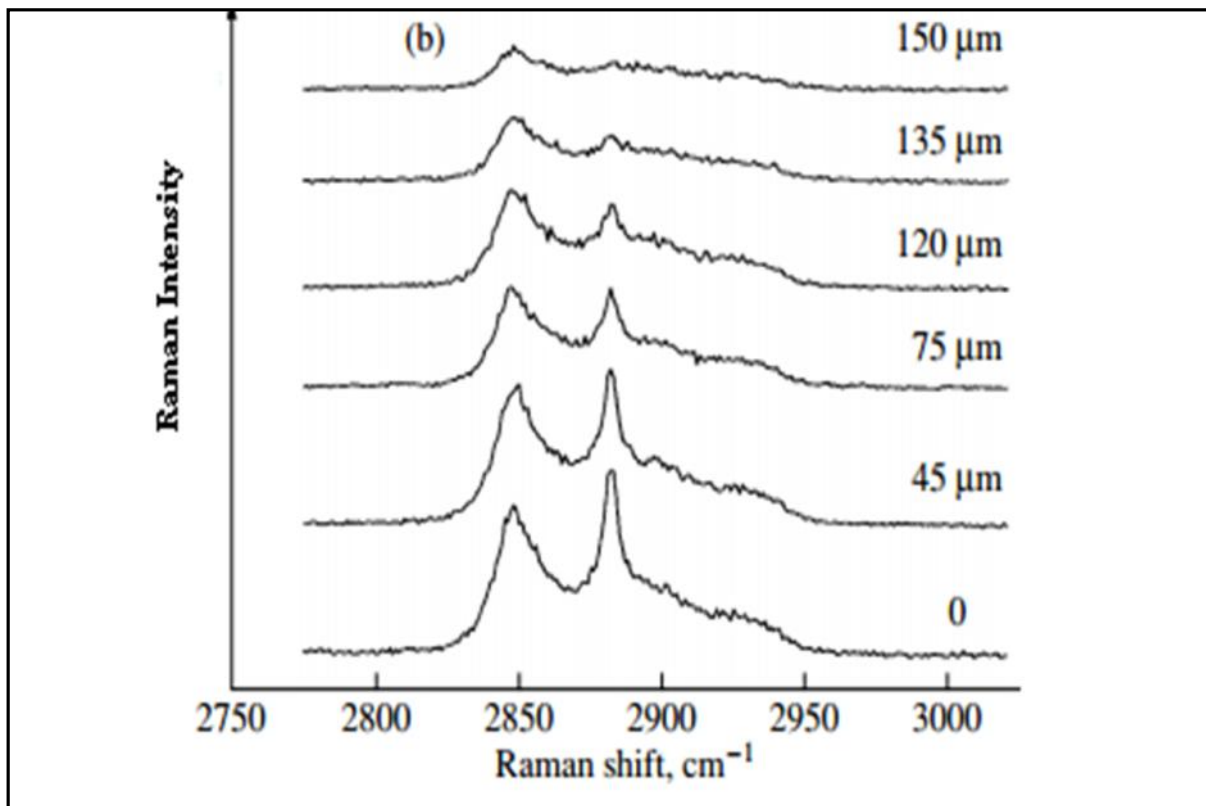


Fig 5: Raman Spectra of Polyethylene bottle at different Sections. [12]

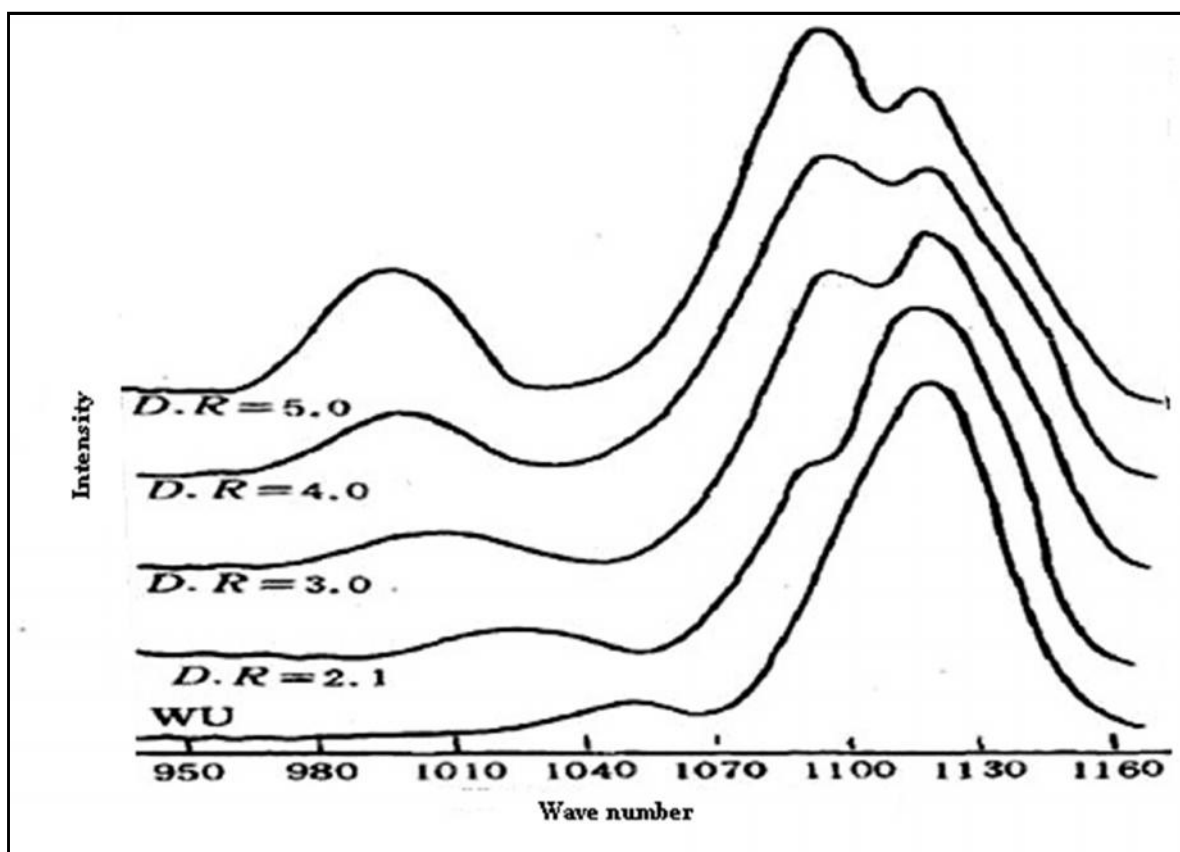


Fig 6: Raman Spectra of samples with different draw ratios. [21]

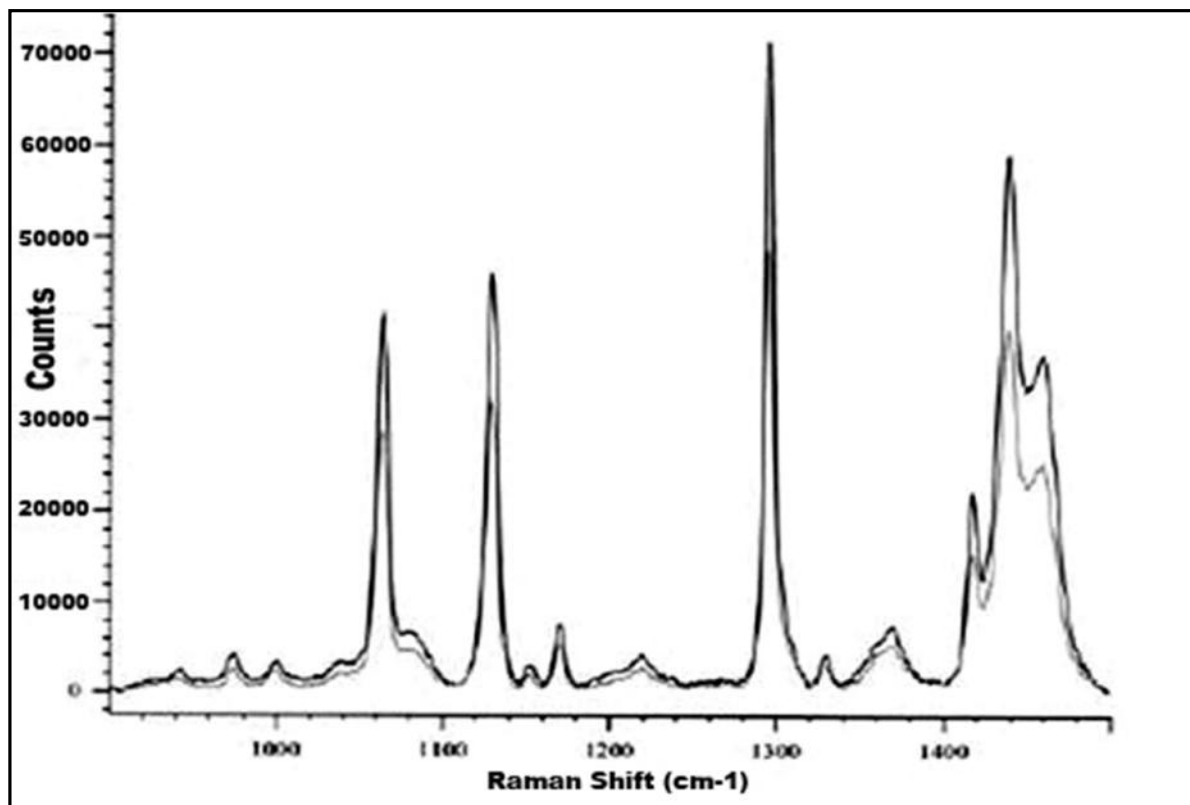


Fig 7(a): Raman Spectra of control film (black) and photo- exposed PE: PP film (gray) from 900 cm^{-1} to 1500 cm^{-1} . [30]

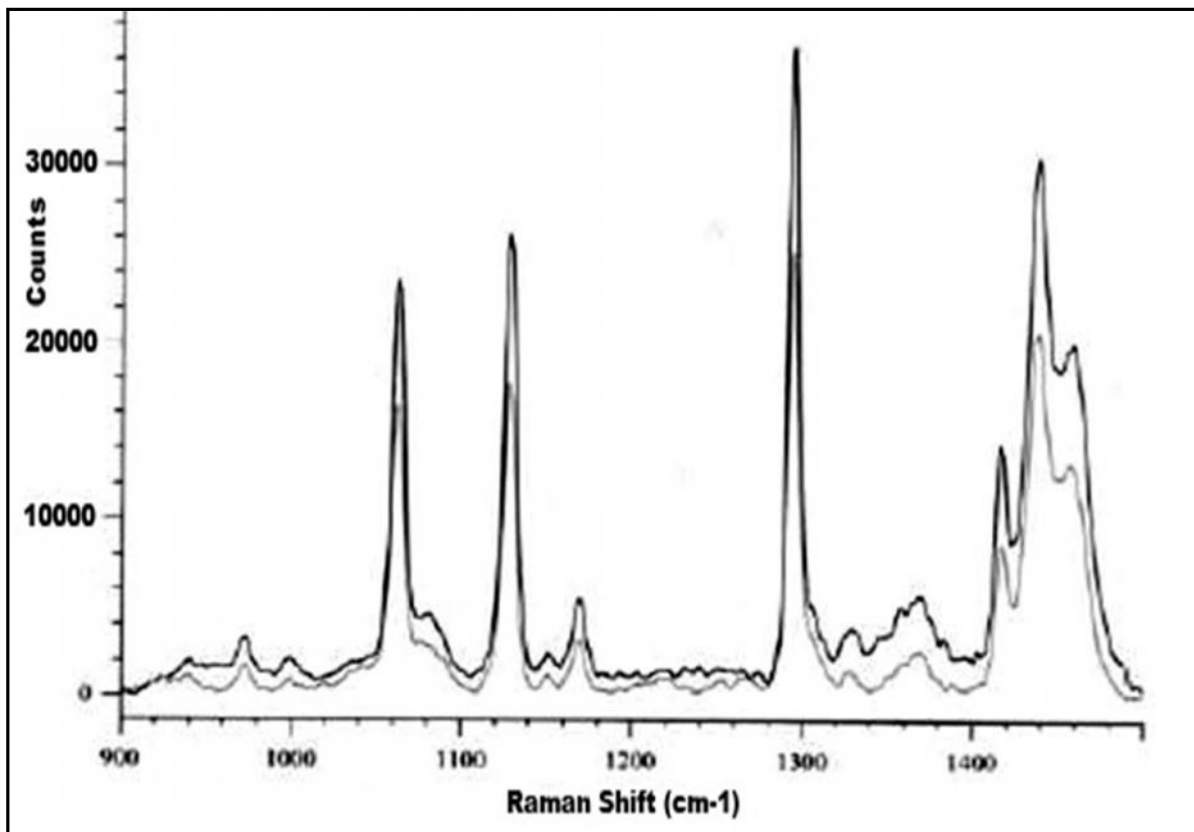


Fig 7(b): Raman Spectra of control film (black) and photo-exposed PE: PP: Clay film (gray) from 900 cm^{-1} to 1500 cm^{-1} . [30]

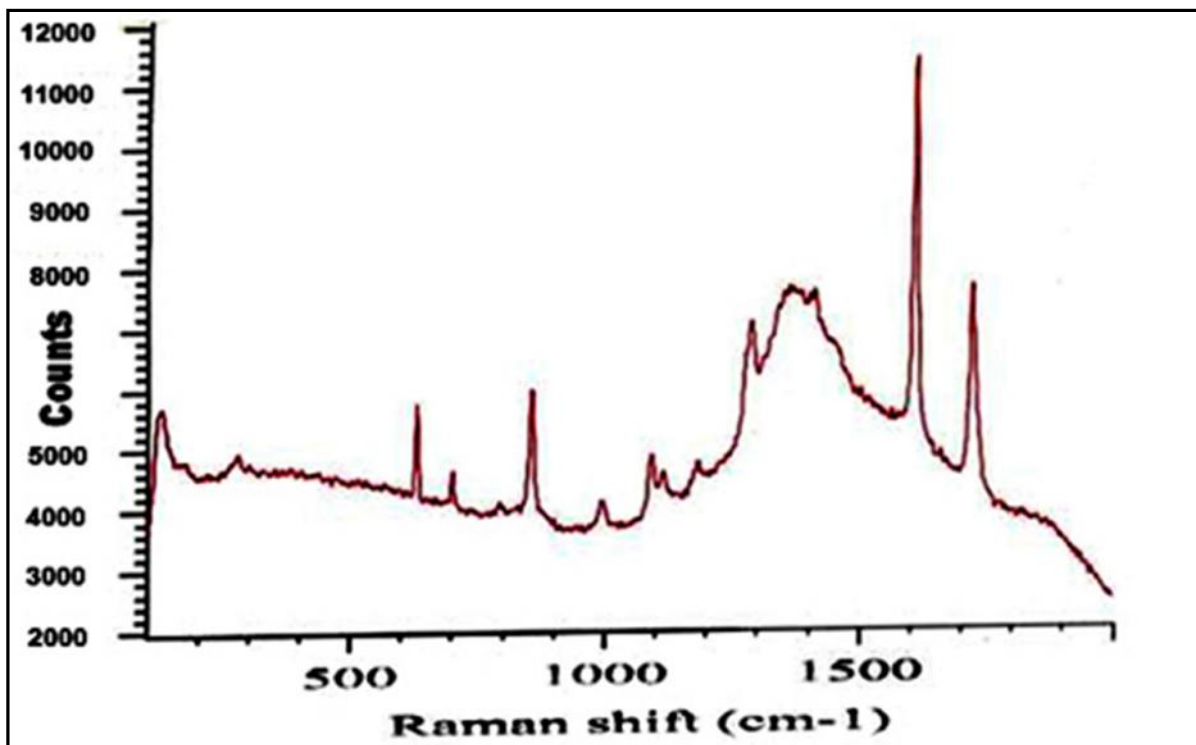


Fig 8(a): Raman Spectra of control 25 μm PET film. [31]

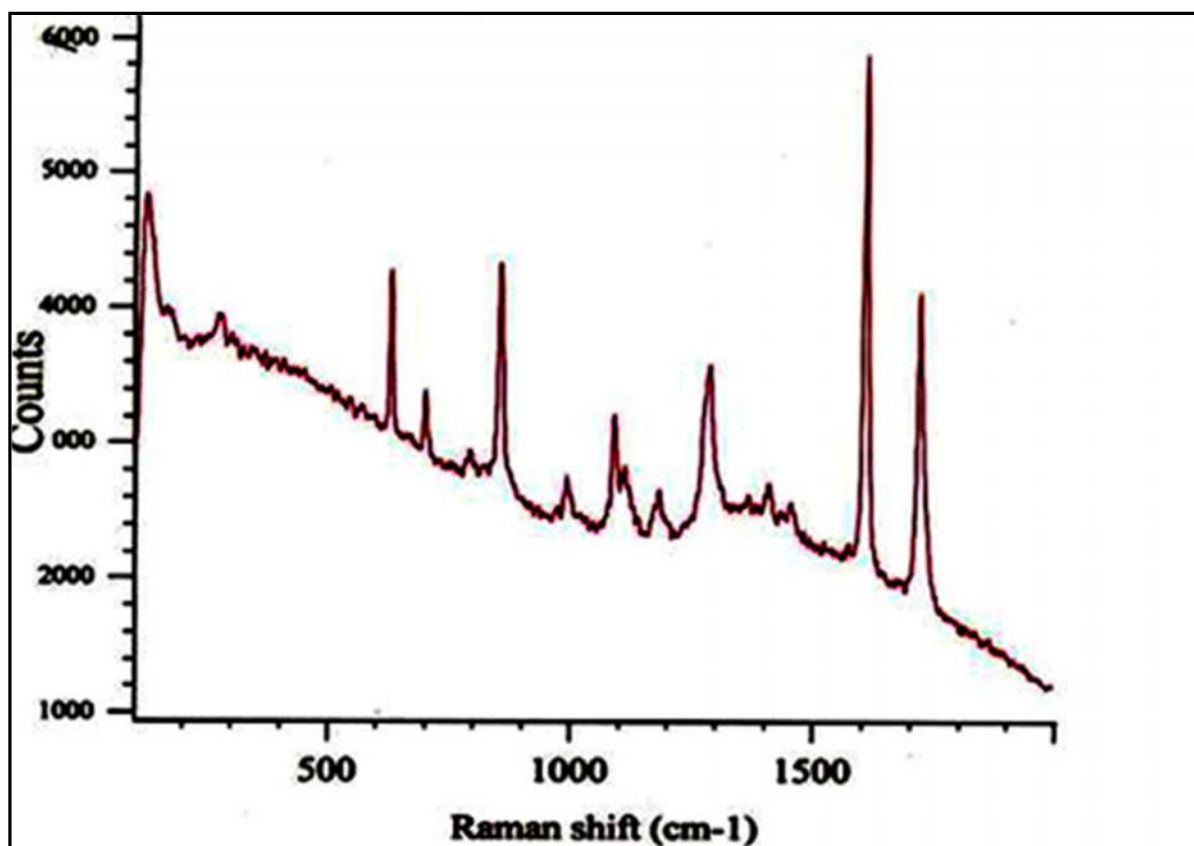


Fig 8(b): Raman Spectra of solar exposed 25 μm PET films. [31]

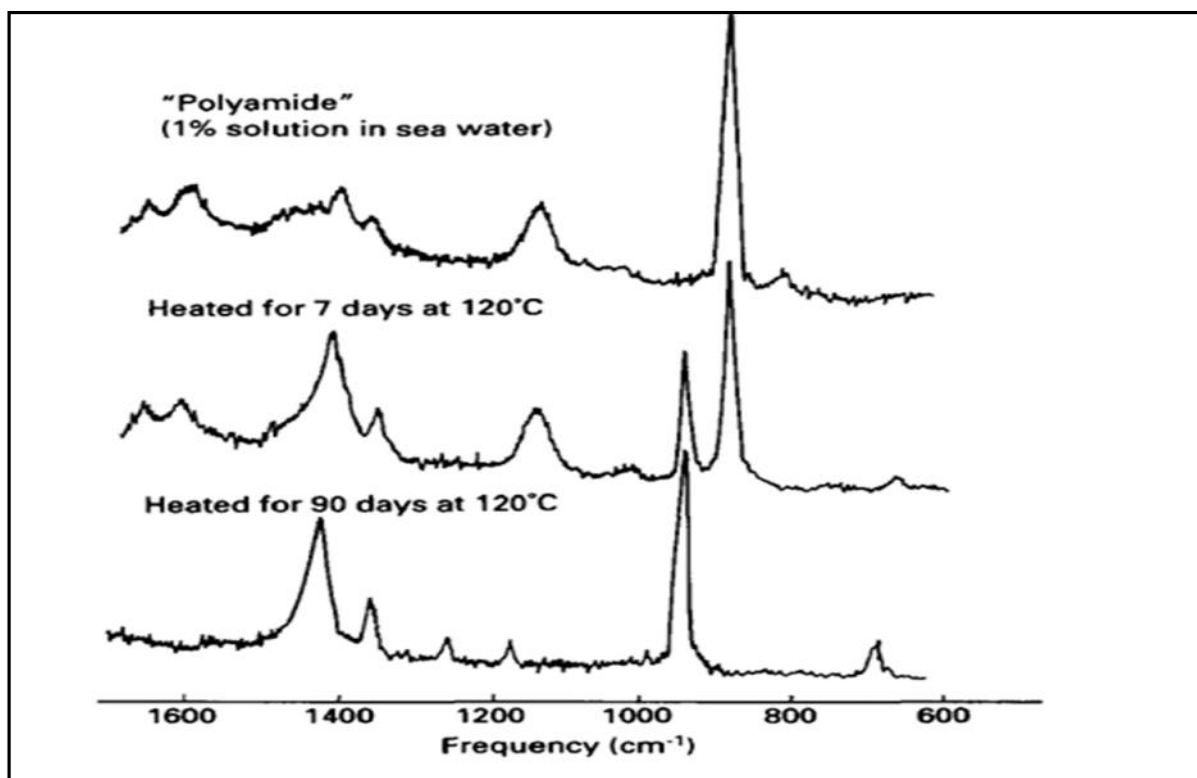


Fig 9: Raman Spectra of a 1% solution of polyamide in sea water, showing the occurrence of hydrolysis as a result of heating at 120°C. [47]

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