Raman Spectroscopic Analyses of Structure–Mechanical Properties Relationship of Crystalline Polyolefin Materials

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Raman spectroscopy is a vibrational spectroscopic technique that is widely used for analyses of the chemical structures and morphologies of polymeric materials. The peak position and peak area of each Raman band are influenced by microscopic deformations of molecular chains, e.g., load-sharing, orientation, and conformational state. In particular, Raman spectroscopic analysis has been used to investigate the structure–mechanical properties relationship of semi-crystalline polyolefins (POs) because the C–C stretching mode, which is the main chain vibration of POs, is strongly Raman-active. The present review summarizes recent Raman spectroscopic analyses of the structure–mechanical properties relationship of POs.

Key Words: Raman spectroscopy / Morphology / Polyolefin / Structure–mechanical properties relationship

1. INTRODUCTION

Polyolefins (POs) such as polyethylene (PE) and polypropylene (PP) are widely used in our daily lives because they are highly drawable, tough, light, and inexpensive. POs have complicated spherulitic morphology composed of lamellar crystalline and amorphous layers that are 10–30 nm thick. Owing to their spherulitic morphology, semi-crystalline polymers exhibit complicated deformation behavior in the solid state under tensile deformation. The spherulitic morphology is transformed into fibrillar morphology during tensile deformation. Although the morphological transformation from a spherulitic to a fibrillar morphology has been widely accepted as a typical deformation model of semi-crystalline polymers, the detailed mechanism by which this transformation takes place has not yet been elucidated. The deformation mechanism of PE and PP have been intensively studied using various mechanical tests and analysis techniques because the superior mechanical properties of PE and PP, such as drawability and toughness, strongly depend on the morphological transformation during tensile deformation.

Vibrational spectroscopic techniques such as infrared (IR) and Raman spectroscopy are powerful methods for investigating the morphologies of various polymers. Rheo-IR spectroscopy, which is a simultaneous measurement of mechanical response and IR spectra, is used to examine the molecular orientation of both crystalline and amorphous chains because the IR measurements can be obtained in a relatively short time (e.g., 1 s). Recently, near-IR (NIR) spectroscopy combined with a tensile test has also been developed. NIR spectroscopy has been applied to the morphological analysis of thick samples because NIR light is highly penetrating.

Raman spectroscopy is one of the most powerful tools for the evaluation of the microscopic deformation behavior of POs because the C–C stretching mode corresponding to the skeletal vibrational mode of POs is strongly Raman-active. In contrast, the C–C stretching mode is inactive in IR and NIR spectroscopies. Therefore, microscopic load-sharing and the molecular orientation of the main chains can be measured directly using Raman spectroscopy. These advantages have led to the use of Raman spectroscopy for evaluating the microscopic deformation behavior of POs.

The present paper is a review of recent developments in analytical techniques and important results concerning the deformation behavior of POs obtained using Raman spectroscopy. There is particular focus on molecular orientation, microscopic load-sharing, and conformational changes during tensile tests.
2. MOLECULAR ORIENTATION

Molecular orientation is one of the most important morphological parameters that affect the mechanical properties of polymeric materials\(^ {28}\). The degree of molecular orientation is evaluated using two orientation parameters \(\langle P_2 \rangle\) and \(\langle P_4 \rangle\) described by:

\[
\langle P_2 \rangle = \frac{3 \cos^2 \theta - 1}{2} \tag{1}
\]

\[
\langle P_4 \rangle = \frac{35 \cos^4 \theta - 30 \cos^2 \theta + 3}{8} \tag{2}
\]

where \(\theta\) is the angle between the molecular chain axis and the stretching direction. \(\langle P_2 \rangle\) is called the Hermans’ orientation coefficient, and represents the average value of the molecular orientation\(^ {29}\). \(\langle P_4 \rangle\) is the 4th moment of the orientation distribution function \(N(\theta)\)\(^ {30,31}\). A plot of \(\langle P_2 \rangle - \langle P_4 \rangle\) is shown in Fig. 1\(^ {29,32}\). In regions (i) and (ii), the molecular chains orient along, and perpendicular to, the stretching direction, respectively. The dashed line shown in regions (i) and (ii) represents the most probable values of uniaxial orientation, which are obtained by maximizing the information entropy of molecular orientation\(^ {31,33}\). Region (iii), where \(\langle P_4 \rangle\) is larger than \(\langle P_2 \rangle\), represents biaxial orientation, and region (iv), where \(\langle P_4 \rangle\) is much lower than \(\langle P_2 \rangle\), represents oblique orientation with the stretching direction.

Both values of \(\langle P_2 \rangle\) and \(\langle P_4 \rangle\) are calculated from polarized Raman intensities measured at various polarization directions of the incident and scattered light\(^ {29}\). Bower proposed a method for calculating these orientation parameters from the polarized Raman spectra measured in five different polarization conditions, and the method provides the most accurate values of \(\langle P_2 \rangle\) and \(\langle P_4 \rangle\)\(^ {27,30,31}\). However, this method cannot be directly applied to in situ measurements of the molecular orientations of films and sheets because both the backscattering and right/left-angle scattering geometries are required to obtain Raman spectra with five different polarization conditions. Frisk \textit{et al.} and Richard-Lacroix \textit{et al.} proposed simplified methods by which orientation parameters can be obtained from Raman spectra with only three polarization conditions, which can be measured in the backscattering geometry, as shown in Fig. 2\(^ {34-36}\). Consequently, these simplified methods enable in situ measurement of the molecular orientation during deformation process by combining Raman spectroscopy with mechanical tests.

Martin \textit{et al.} developed a real-time Raman spectroscopic system combining Raman spectroscopy and the VideoTraction\textsuperscript{TM} system that enables the simultaneous acquisition of true stress–true strain curves and Raman spectra\(^ {37}\). According to their results, the orientation functions of the molecular chains in the crystalline and amorphous structures of PP were calculated from the polarized intensities of the Raman bands. The crystalline chains orient markedly to the stretching direction beyond the yield point, whereas the

![Fig. 1](a) \((P_2)-(P_4)\) diagram, and (b) typical molecular orientation distributions at regions (i) to (iv).

![Fig. 2](Schematic of the backscattering geometry of a Raman spectroscopic system.)
orientation function of the amorphous chains immediately increases in the elastic region and reaches an asymptotic value in the strain-hardening region\(^\text{37}\). Kida et al. measured the strain dependences of both orientation parameters and the orientation distribution function of crystalline chains during the uniaxial elongation of various PE samples\(^\text{38-41}\) at various temperatures\(^\text{42}\). For high-density PE (HDPE) with a crystallinity of more than 60 vol\%, the values of \(\langle P_2 \rangle\) and \(\langle P_4 \rangle\) during the yield deformation are in the region (iv): the values of \(\langle P_4 \rangle\) decrease in the yield region, whereas \(\langle P_2 \rangle\) increases monotonously with increasing strain. This result suggests that the crystalline chains orient to the oblique direction (\(\theta = 30–50^\circ\)) even during uniaxial stretching\(^\text{38-41}\). Oblique orientation of the crystalline chains has been observed in both PE and PP\(^\text{43}\), and is caused by the suppression of the molecular orientation due to the excluded volume effect of the rigid and bulky lamellar structure\(^\text{44}\). The oblique orientation observed as the lower deviation from the most probable curve (the dashed line) is commonly observed for HDPE samples with different molecular weights and molecular weight distributions, as shown in Fig. 3(a) and (b). The orientation degree of crystalline chains depends on its molecular weight and molecular weight distribution: samples with lower \(M_w\) or higher \(M_w/M_n\) values have a high degree of molecular orientation in the stretching direction with uniaxial stretching behavior\(^\text{40, 41}\). On the other hand, the values of \(\langle P_2 \rangle\) and \(\langle P_4 \rangle\) lie in the dotted curve above 60 °C, which represents an ideal uniaxial orientation, as shown in Fig. 3(c)\(^\text{42}\). Considering that \(\alpha_1\) relaxation corresponding to the intercrystalline relaxation is observed at around 60 °C for PE\(^\text{42, 45, 46}\), the size of the fragmented lamellar crystals above 60 °C is smaller than that below 60 °C, which results in the ideal uniaxial orientation of the crystalline chains. The \(\langle P_2 \rangle - \langle P_4 \rangle\) curves of ultra-low-density PE (ULDPE) and PE gels composed of HDPE and liquid paraffin are located in the biaxial orientation region (iii) during uniaxial tensile deformation, and are shown in Fig. 3(d)\(^\text{39, 47}\). In the case of ULDPE, the lamellar crystals located in the polar region in spherulites remain in their perpendicular orientation during uniaxial deformation because the stretching stress is weakly transmitted to the lamellar crystals owing to low crystallinity\(^\text{39}\). PE gels composed of HDPE and liquid paraffin have a cellular structure in which the cells comprise lamellar crystals and the pores comprise liquid paraffin. The cellular structure is strained along the stretching direction and the lamellar crystals in the wall of the cellular structure are fragmented into small crystals, then oriented to the stretching direction. However, the lamellar crystals aligned to the stretching direction, which are located in the...
walls of the cellular structures of the equatorial region, are not deformed during the stretching process, resulting in biaxial orientation\(^4\). These results suggest that crystalline chains have complicated orientation behavior even under simple uniaxial tensile deformation, which should influence the mechanical response of the polymer.

### 3. MICROSCOPIC LOAD-SHARING

The peak position \((\nu)\) of IR and Raman bands is determined by the spring constant of the molecular vibration \((k)\):

\[
\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}
\]  

(3),

where \(c\) is the speed of light and \(\mu\) is the reduced mass. The value of \(k\) increases or decreases according to the applied compression or stretching load on the molecular chains, respectively. Therefore, a positive or negative peak shift indicates that compression or stretching load has been applied to the molecular chains, respectively. Wool \textit{et al.} demonstrated that the peak shift has a linear relationship with the stress applied to the specimen in the elastic region that can be described by\(^{26, 48}\):

\[
\Delta \nu = \nu(\sigma) - \nu(0) = \alpha \sigma
\]  

(4),

where \(\sigma\) is the stress applied to the specimen, \(\nu(\sigma)\) is the peak position at each applied stress, and \(\alpha\) is the peak shift factor. The slope of the peak shift plotted against the applied stress corresponds to \(\alpha\). The value of \(\alpha\) strongly depends on the molecular vibration, as shown in Fig. 4.\(^{26, 49-51}\). It should be noted that the peak shifts shown in Fig. 4 were measured using a drawn specimen with highly oriented molecular chains. For example, the C–C stretching mode, which corresponds to the molecular vibration of the backbone of the molecular chains, is associated with a high value of \(\alpha\) because the applied stress is directly transmitted to the skeletal chains. Conversely, molecular vibrations such as CH\(_2\) twisting and rocking modes are associated with low \(\alpha\) values compared with the C–C stretching mode because molecular vibrations of the pendant groups remain practically constant with regard to the load-sharing of the molecular chains\(^{49, 50}\). The peak shift attributable to pendant-group molecular vibrations is very sensitive to interchain interactions compared with that attributable to main-chain vibrations\(^{52, 53}\), so pendant-group vibrations are strongly influenced by structural changes such as crystal lattice expansion\(^{54}\) and disordering of the crystal structure\(^{40, 55}\). Real-time measurement of peak shift during tensile deformation is a powerful method of accurately evaluating the microscopic load-sharing of the molecular chains, because the stress applied to the molecular chains is immediately relaxed after deformation ceases. Hiejima \textit{et al.} demonstrated that the peak shift of Raman bands immediately recovers to zero at the beginning of stress relaxation\(^{56}\).

The rheo-Raman spectroscopic system was first developed by Siesler \textit{et al.}\(^{57}\), and Pastor \textit{et al.} used a similar system to investigate microscopic load-sharing during tensile tests on PE\(^{58}\) and PP\(^{59}\). They demonstrated that the stretching load is applied to the crystalline chains beyond the yield region and the load increases with increasing strain. Recently, Kida \textit{et al.} also investigated the load-sharing of the crystalline chains from the peak shifts of the anti-symmetric and symmetric C–C stretching modes observed at 1063 and 1130 cm\(^{-1}\), respectively, of the crystalline chains of PE\(^{38, 42, 51}\). Because the vibrational directions of the anti-symmetric and symmetric C–C stretching modes are along and perpendicular to the molecular chain axis of the crystalline chains, the heterogeneity in the load sharing of the crystalline chains can be detected using these Raman bands. The compression load is applied perpendicular to the molecular chain axis of the
crystalline structure during yield deformation, whereas the stretching load is simply applied along the molecular chain axis. This heterogeneous load-sharing during yield deformation is also observed in isotactic polypropylene (iPP)43. Nitta and Takayanagi proposed that the lamellar cluster units, which are composed of a few stacked lamellar crystal layers, are formed as mobile units during uniaxial stretching44, 60). These cluster units are approximately 30–50 nm in size, as determined by the weight-average molecular weight. Considering that the lateral shrinkage of a specimen occurs during necking due to the Poisson’s effect61), the compression load applied perpendicular to the crystalline chains is caused by the suppression of the lateral shrinkage due to the excluded volume effect of rigid and bulky lamellar cluster units. Moreover, the stretching load applied to the crystalline chains increases with increasing molecular weight, whereas load-sharing is independent of the molecular weight distribution41). The effects of the molecular weight and its distribution suggest that the microscopic load-sharing of molecular chains strongly depends on the size of the lamellar cluster units, because the size of those units increases with increasing molecular weight, although it is independent of the molecular weight distribution41, 62).

The peak shift of crystalline chains in highly oriented films and fibers is accompanied by a broadening of the bandwidth and/or separation of one band under stretching stress63, 64). In one study on fibers, the Raman band at 1063 cm\(^{-1}\) assigned to the C–C stretching mode broadened as the applied stress increased, and separated into two bands at high stretching stress of 2.07 GPa, as shown in Fig. 565). If the stress applied to a specimen is homogeneously propagated through the molecular chains, the peak shift should occur without the broadening and separation of each band. Consequently, the broadening and separation of a Raman band accompanied by stretching stress suggests inhomogeneous stress distribution. Inhomogeneous stress distribution is analyzed using a mechanical equivalent model combined with continuous crystalline, dispersed crystalline, and amorphous components, as shown in Fig. 6. The stresses applied to the continuous and dispersed crystalline structures are described by\(^{66, 67)}\):

\[
\sigma_{cc} = \sigma \tag{5}
\]

\[
\sigma_{dc} = \frac{E_c}{\lambda E_c - (1 - \lambda)E_a} \sigma \tag{6}
\]

where \(\sigma_{cc}\) and \(\sigma_{dc}\) are the applied stresses on the continuous and dispersed crystalline structures, respectively. \(\sigma\) is the applied stress on a specimen. \(E_c\) and \(E_a\) are the moduli of the crystalline and amorphous regions (281 GPa\(^{68}\) and 0.5 GPa\(^{69, 70}\)), respectively. According to equation (6), \(\sigma_{dc}\) should be much higher than \(\sigma\) because \(E_a\) is much lower than \(E_c\). Based on the mechanical equivalent model, the broadening and separation of each band by the applied stress are caused by the larger peak shift of the dispersed crystalline structure than that of the continuous crystalline structure, as shown in Fig. 7. Tashiro et al. demonstrated a quantitative evaluation of the fraction of the dispersed crystalline component from the combined analysis of the peak shift of the 1063 cm\(^{-1}\) band and the mechanical equivalent model\(^{71)}\). According to their results, the fraction of the dispersed crystalline component was approximately 0.2 wt% of the PE.

![Fig. 5](image_url) Raman spectra of a polyethylene (PE) fiber under various stretching stresses. (From K. Prasad and D. Grubb, J. Polym. Sci. Part B: Polym. Phys., 1989, 27, 381, ©1989 John Wiley & Sons, Inc., reproduced by permission.)

![Fig. 6](image_url) Schematic of the mechanical-equivalent model comprising continuous crystalline, dispersed crystalline, and amorphous components. \(\phi\) and \(1 - \phi\) denote the crystallinity and fraction of dispersed crystalline structure, respectively.
fiber. Considering that the taut-tie chains of PE are consisted of the consecutive trans sequences as same as the crystalline chains for PE, the dispersed crystalline component may be attributed to the taut-tie chains. Peak shift analysis of the Raman band is an important method for evaluating the stress distribution of molecular chains, which cannot be achieved using other analytical techniques.

4. CONFORMATIONAL CHANGES

As with IR spectroscopy, the intensity of Raman bands is sensitive to the conformational state of the molecular chains. In particular, the fraction of molecular chains in the intermediate state between crystalline and amorphous structure, which is difficult to detect using other typical approaches such as X-ray scattering, can be directly obtained using vibrational spectroscopic techniques.

The assignments of typical Raman bands of PE are listed in Table I. The Raman band at 1418 cm\(^{-1}\) is attributable to the crystal field splitting of the CH\(_2\) bending mode in an orthorhombic crystalline cell that includes two methylene units. Consequently, the orthorhombic crystalline fraction (\(\chi_C\)), which corresponds to the crystallinity of PE, can be determined by the peak area of the 1418 cm\(^{-1}\) band using the following equation:

\[
\chi_C = \frac{I_{1418}}{0.46(I_{1298} + I_{1305})}
\]  

where \(I_i\) denotes the integrated intensity of Raman band at each wavenumber \((i)\). Here, the sum of the intensities of Raman bands at 1298 and 1305 cm\(^{-1}\) is used as the internal reference because the sum of these bands is independent of temperature. The anti-symmetric and symmetric C–C stretching modes, which appear at 1063 and 1130 cm\(^{-1}\), respectively, are assigned to the long consecutive trans sequences of more than 10 trans conformers, whereas the CH\(_2\) twisting mode appears at 1298 cm\(^{-1}\), and is assigned to the consecutive trans sequences of more than 3 to 5 trans conformers. The fractions of long consecutive trans sequences (\(\chi_{LCT}\)) and consecutive trans chains (\(\chi_{CT}\)) are described by:

\[
\chi_{LCT} = \frac{I_{1130}}{0.89(I_{1298} + I_{1305})}
\]  

\[
\chi_{CT} = \frac{I_{1298}}{I_{1298} + I_{1305}}
\]

\(\chi_{LCT}\) is close to the crystallinity because the long consecutive trans sequences are mostly located in crystalline chains for various PEs. Migler et al. proposed that the taut-tie chains, which are the non-crystalline long consecutive trans sequences, also contribute to the intensity of 1063 and 1130 cm\(^{-1}\). The consecutive trans sequences of more than 3 to 5 trans conformers are located in both crystalline and amorphous structures. Thus, the fraction of non-crystalline consecutive trans (NCCT) chains (\(\chi_{NCCT}\)) is calculated from the difference between the fraction of consecutive trans sequences and the orthorhombic crystallinity using the following equation:

\[
\chi_{NCCT} + \chi_{CT} = \chi_C
\]

In general, NCCT chains have been attributed to the transition region of the crystalline and amorphous layers and/or disordered crystalline structure. Figure 8 summarizes the crystalline, amorphous, and NCCT chains. Conformational changes during uniaxial stretching are determined by introducing an appropriate correction for molecular orientation. Lagaron et al. proposed an accurate method for evaluating the crystallinity and fraction of trans sequences by removing the influence of molecular orientation from the intensity of each band. They demonstrated that the crystallinity decreased by approximately 20% for a
drawn HDPE specimen using the evaluation method, although the fraction of long consecutive trans sequences showed no change. Kida et al. applied the Lagaron’s method for in situ measurement under tensile deformation: the crystallinity decreased markedly as the strain increased beyond the yield point, whereas the fraction of the long consecutive trans sequences was almost the same during tensile deformation. These results suggest that orthorhombic crystalline regularity becomes disordered due to fragmentation of lamellar crystals in the yield deformation but the consecutive nature of the trans sequences is retained. Bates et al. carried out an in situ measurement of the number of consecutive trans sequences and amorphous chains in linear-low-density PE (LLDPE). According to their results, the fraction of consecutive trans sequences increased markedly in the elastic region; this was followed by a plateau region beyond the yield point, which was similar to the strain dependence on molecular orientation. These results are in good agreement with the typical deformation model that the tie chains connecting the adjacent lamellar crystalline layers are elongated into the stretching direction in the elastic region.

The intensities of some Raman bands of PP are very sensitive to the length of the helical chains. For example, Raman bands at 973, 998, 841, and 1220 cm$^{-1}$ are assigned to consecutive helical chains with more than 5, 10, 12, and 14 monomer units, respectively. The assignments of the typical Raman bands of PP are listed in Table II. Considering that the minimum length of the crystalline layer of PP is approximately 2.38 nm, helical chains with more than 12 monomers correspond to the crystalline chains. Comparisons of the temperature dependences of the number of helical chains having different lengths have been used to elucidate the crystallization behavior of PP. However, the evaluation of the conformational state of PP during tensile deformation has not been reported, owing to the difficulty of removing the influence of molecular orientation from the intensity of each Raman band. Considering that the crystalline structure features complicated structural changes such as the formation of a mesophase under tensile deformation, the evaluation of the number of helical chains of a specific length will facilitate elucidation of the deformation mechanism in PP.

5. CONCLUSIONS

A Raman spectrum provides various information about microscopic deformation behavior, such as the load-sharing, molecular orientation, and conformational changes of polymeric materials. The orientation distribution function is calculated from two orientation parameters obtained from the polarized Raman intensities. Various molecular orientation states, such as uniaxial, biaxial, and oblique orientations, can be accurately evaluated using the orientation distribution function. An evaluation of the molecular orientation distribution facilitates an understanding of the molecular orientation behavior of polymeric materials with complex supermolecular structures, such as spherulitic morphology and cellular structure, because deformation of the supermolecular structure leads to biaxial and oblique orientation to the stretching...
direction, even under uniaxial stretching. The peak shift of each Raman band is influenced by the load-sharing of the molecular chains. The heterogeneity of the load-sharing of the molecular chains can be evaluated by combining peak shifts of molecular vibrations in different directions. Moreover, the combined analysis of the peak shift and the mechanical-equivalent model is a powerful analytical technique for the evaluation of stress distribution of molecular chains, which is difficult using other analytical methods. The fraction of molecular chains with each conformational state can be quantitatively determined using IR and Raman spectroscopy. In particular for PE and PP, the length of consecutive trans sequences or helical chains can be quantitatively determined using IR and Raman spectroscopy. In particular for PE and PP, the length of consecutive trans sequences or helical chains can be evaluated from the intensity of each Raman band. Considering that disordering and/or crystalline transformation occur during yield deformation for various semi-crystalline POs, such evaluation of the fractions of molecular chains in different conformational states is important for the elucidation of the microscopic deformation mechanism. These analytical techniques for investigating structure–mechanical properties relationship can also be applied to various polymeric materials in both solid and liquid states. For example, evaluation of the microscopic deformation behavior by Raman spectroscopy can facilitate the improvement of the mechanical properties of biodegradable polymers that have poor drawability and toughness compared with POs. Moreover, the development of simultaneous measurements using a Raman microscope and mechanical tests will provide valuable information about mechanical properties, such as the distribution of the strength of interfaces of polymer blends and the location dependence of the deformation behavior of lamellar crystals in spherulites.

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