International Journal of Applied and Advanced Scientific Research (IJAASR)
Impact Factor: 5.655, ISSN (Online): 2456 - 3080
(www.dvpublication.com) Volume 3, Issue 1, 2018

APPLICATION OF RAMAN SPECTRA IN QUANTITATIVE ANALYSIS OF POLYPROPYLENE / CYCLIC OLEFIN COPOLYMERS BLENDS

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Cite This Article: Aravinthan Gopanna, Selvin P. Thomas, Krishna Prasad Rajan & Murthy Chavali, "Application of Raman Spectra in Quantitative Analysis of Polypropylene / Cyclic Olefin Copolymers Blends", International Journal of Applied and Advanced Scientific Research, Volume 3, Issue 1, Page Number 338-344, 2018.

Abstract:

Polypropylene (PP) and cyclic olefin copolymers (COC) were blended over full composition range by melt mixing technique using a co-rotating twin-screw extruder. Raman spectroscopy investigations on Polypropylene, cyclic olefin copolymers, and its blends are reported. The ratio of the integral intensities of polypropylene and cyclic olefin copolymers fundamental vibrations is used to determine the blend contents for complete composition range.

Key Words: Raman Spectroscopy, Polypropylene, Cyclic Olefin Copolymers & Polymer Blends

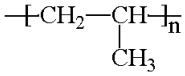
Introduction:

Two or more polymers are blended together for the improvement of their characteristics than those of individual polymers and also for the development of cost-effective materials with novel properties and applications. The characteristics of polymer blends depend on its components - content, molecular weight, structure, crystallisability, compatibility, etc. The potential application of blend materials depends on their combined mechanical, thermal, chemical and other physic-chemical properties [1]. However, careful choice of parent polymers especially their compatibility with each other still remains one of the most important aspects for the blend materials to show superior properties. With this respect, polypropylene and cyclic olefin copolymers offer significant promises for the development of such blend materials.

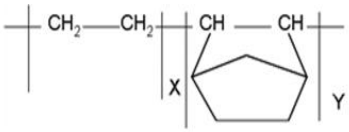
Polypropylene (PP) is one of the multi-purpose plastics extensively used in the fabrication of domestic and industrial products (2). In addition to being low cost and light weight materials, polypropylene also has excellent rigidity/impact balance, moderate strength, outstanding fatigue resistance, superior chemical resistance, good steam barrier, etc [3]. Cyclic olefin copolymers (COC) are amorphous transparent plastics, copolymerized from ethylene and 2-norbornene with a metallocene catalyst, suitable for the fabrication of transparent products, drugs packaging, food containers, medical appliances, diagnostic devices, etc. Cyclic olefin copolymers have remarkable characteristics such as superior transparency, high glass transition temperature, excellent mechanical properties, good heat resistance, chemical resistance to common solvents, low moisture uptake, etc [4].

The blending of polypropylene and cyclic olefin copolymers over the entire composition range from PP100:COC0 to PP0:COC100 with the increment of 10% COC fraction by melt mixing technique was carried out without using any compatibilizer due to the olefinic components of both polymers. While, the fraction of COC component in the blends with fibrous structures determines mechanical strength of the blend, amorphous cyclic olefin copolymer component affects the crystallisation processes of polypropylene based on its content and the volume distribution [5-9]. Despite such progress in the field especially regarding the properties of the blend, the mechanistic evaluation of the blending process via meltmixing techniques still remain an area of concern due to lack of techniques for monitoring conversions. Thus a non-destructive, simple monitoring technique is always welcome to further explore the system and in this case, Raman spectroscopy became useful.
Raman spectroscopy is a non-destructive, effective and convenient method for the structural analysis of organic, inorganic and biological materials. Raman spectroscopy provides both qualitative and quantitative information of samples such as percent composition, crystallinity, stereo-regularity, phase transitions, and polymorphs (10). In general, Raman spectrometers are based on two different technologies such as dispersive Raman and Fourier transform Raman. The dispersive technique is the best choice for investigation of small particles and constituents due to its higher sensitivity, resulting in stronger signal and higher spatial resolution as well as the fact that it operate at visible wavelengths [10-13]. Among the available applications, Raman spectroscopy is routinely used for identification and quantification of polymers and polymer blends because no two polymers

give exactly the same Raman spectra and the intensity of the scattered light is proportional to the amount of component composition in the blends. However, there is no information about Raman spectra of polypropylene/cyclic olefin copolymers (PP/COC) blends in the literature. The main objective of this work is to study the Raman spectroscopy of PP, COC, and PP/COC blends as well as quantitative analysis of the blends based on the ratio of the integral intensity of fundamental vibrations of PP and COC.



Molecular structure of PP



Molecular structure of COC

Experimental Methods:

Materials:

Commercial grades of PP (TELDENE, grade B20ML) density: 0.905 g/cm^3, MVR: 1.5 cm^3/10 min and COC (TOPAS, grade 6017S) density: 1.020g/cm^3, MFR: 21 g/10minwere acquired from NATPET (Saudi Arabia) and TOPAS Advanced Polymers (Germany) respectively.

Blending:

PP and COC pellets were manually mixed in the ratios of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 in which the numbers represent the weight percentages of PP and COC, respectively. The mixtures were melt blended using co-rotating intermeshing twin screw extruder (HAAKE, RheomexPTW24/40-MC OS, Germany) with L/D of 40 (24mm screw diameter). The screw speeds were maintained at 200 rpm and the barrel temperatures ranging from 180°C at the feed zone to 260°C at the metering and die zones. The extruded strands were water cooled and pelletized. The extruded pellets were properly dried and moulded into rectangular shaped specimen (L80XW10XT4 mm) using the injection moulding machine (Haake Minijet II, Germany). Injection moulding was carried out at cylinder temperature 280^{0}C under 300 bar of injection pressure for 10 s. Neat PP and COC samples also prepared for the comparison in the similar procedure. The neat polymers and blends were denoted as PP100, COC10, COC20, COC30, COC40, COC50, COC60, COC70, COC80, COC90 and COC100 (PP100 = 100 % PP polymers and COCx = x weight % of COC polymers mixed with 100-x weight % of PP polymers).

Raman Spectroscopy:

DXR Raman Microscope (Thermo Scientific, USA) was employed to carry out the Raman Spectroscopy measurement of the samples. In the operation, the laser beam was focused using an objective lens on the sample and the scattered radiation from the sample was directed into the imaging spectrometer through a collection lens and Raman spectra were recorded as examined by the charge coupled device (CCD) detector by using appropriate Rayleigh filters and automated aperture selection. A 780 nm laser source and 780 full range grating were used. The Raman spectra were measured at 50 µm pinhole aperture with a spectral resolution of 4.7 cm^{-1}to 8.7cm^{-1}. For neat polymers and blends, the flat surface of the rectangular shaped sample was fixed on the sample holder for data recording.

Experimental Results and Discussions:

Raman Spectrum of PP:

Figure 1 shows the Raman spectrum of neat PP. In Raman spectrum of PP, peaks are observed between 500 and1500cm^{-1}and also from 2600to 3000cm^{-1}. The Raman spectrum of PP from 500 to 1500cm^{-1} includes C–C stretching vibrations, CH_2 deformation and CH_3 deformation vibrations and from 2600to 3000cm^{-1} includes CH_2 and CH_3 stretching vibrations. The intensities of C–C stretching vibrations, CH_2deformation, and CH_3 deformation vibrations are considerably less than the intensities of CH_2 and CH_3stretching vibrations. The additional bands appeared from500 to 1500 cm^{-1}range are recognised to the 3_1 helix, which is the normal conformation in isotactic polypropylene polymorphs and mesomorphic phase [14].

Raman peaks at 810, 842, 901, 999, 1168and 1220 cm^{-1} show highly regular helical sequences that are associated with crystalline domains. Raman peaks at 810 and 842 cm^{-1}are due to the vibrations of molecules in the crystalline phase and the vibrations of helical molecules contained in the amorphous regions respectively. The ratio of842 to 810 cm^{-1} band intensity is used to measure the molecular orientation in PP. The bands observed at 999 and 842cm^{-1}are for helical segments with at least 11 and 14 repeating units respectively. Additionally, the shorter helical segments are recognised at 974 cm^1 bands. The ratio of peak area at 999cm^{-1} band to the peak area at 974cm^{-1} bands is used as isotacticity index [14]. Raman peaks at 974and 1153 cm^{-1} are assigned to the rocking mode of CH_3group. The band at 1168 cm^{-1} is allocated to the stretching of C-C in the backbone, which is related to the stress-sensitive molecular deformation [14-21]. Table 1 summarises the assignments of Raman bands of PP [22, 23].

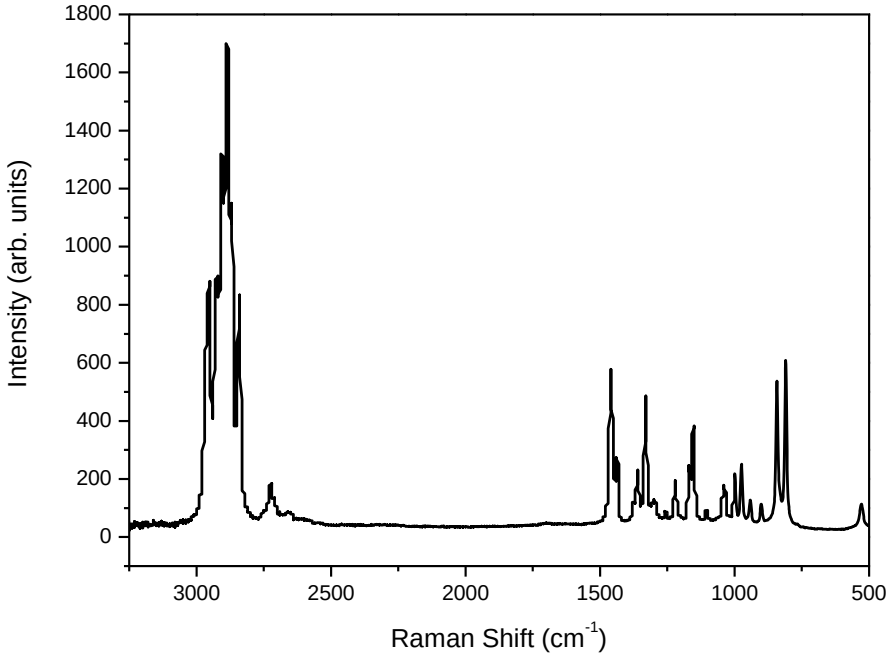


Figure 1: Raman spectrum of PP

Table 1: Band assignments in the Raman spectrum of PP

Raman Frequency cm^{-1}	**Vibration Mode**
810	CH_2 Rocking, C-C Stretching
842	CH_2 Rocking
974	CH_3 Rocking, C-C Stretching
999	CH_3 Rocking
1153	C-C Stretching, CH Bending
1168	C-C Stretching, C-C wagging , CH_3 Rocking
1220	CH_2 Twisting, CH wagging, C-C Stretching
1330	CH Bending , CH_2 Twisting
1437	CH_2Bending
1459	CH_2Bending

Raman Spectrum of COC:

Figure 2 shows the Raman spectrum of neat COC. According to John Forsyth et al., the strong bands observed at 749, 889 and 932 cm^{-1} corresponds to norbornene units in COC [24]. In the COC spectrum, the bands at 749 and 932 cm^{-1} represented the ring vibrations of COC molecules. The ringbreathing mode of COC molecules is observed in Raman spectrum region at 889 cm^{-1}. Typically for polyethene, amorphous and crystalline region peaks observed at 1075 and 1062 cm^{-1} respectively. Due to amorphous characteristics of COC, only 1075 cm^{-1} peak is observed in neat COC Raman spectrum. Moreover the sharp peak at 1416 cm^{-1} is characterised for an orthorhombic crystal structure in polyethylene (24). The absence of this peak in the COC Raman spectrum shows that there is no crystalline domain within the sample associated with the existence of ethylene block [24, 25]. Raman peaks at 1225and 1311 cm^{-1} are related to the twisting mode of theCH_2group in COC. Table 2 summarises the assignments of Raman bands of COC [22, 23].

Table 2: Band assignments in the Raman spectrum of COC

Raman Frequency cm^{-1}	**Vibration Mode**
889	CH2 Rocking
932	Ring Vibration
1075	C-C Stretching
1225	CH_2 Twisting
1448	CH2 Bending

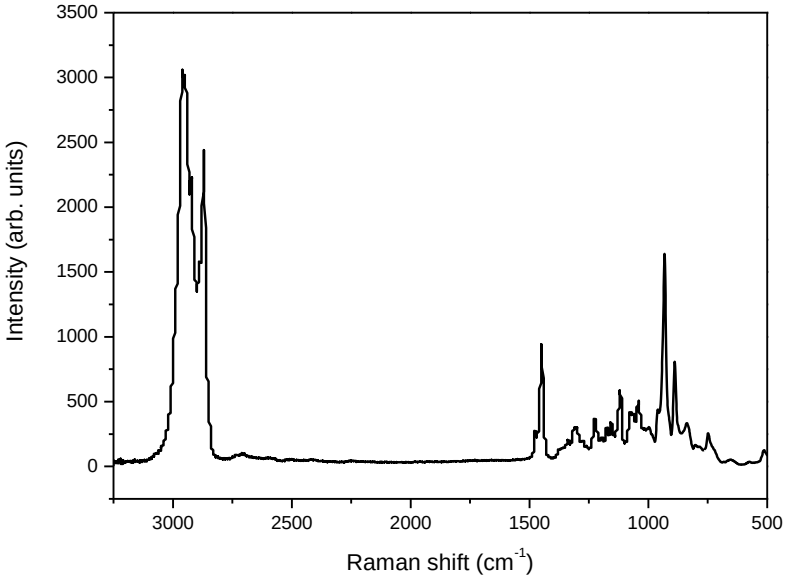


Figure 2: Raman spectrum of COC

Raman Spectra of PP/COC Blends:

Figure 3 shows the Raman spectra of the PP/COC blends as well as neat PP and COC that are used for the melt mixed PP/COC blends. De Baezet al. stated that the degree of crystallinity increases in polypropylene, as the intensity of the peak at 810cm^{-1} increases relative to the intensity of the peak at 842cm^{-1}[26].In PP rich PP/COC blends, it is observed that the intensity of 810 cm^{-1} band is high as compared to the intensity of the842cm^{-1}band, supporting the previous report. Similarly, in COC rich PP/COC blends, the intensity of the peak at 810 cm^{-1} decreases, compared to the intensity of the peak at 842cm^{-1}.As the content of COC increases, the ring vibration and ring breathing intensities corresponding to COC molecules are enhanced in the PP/COC blends.CH_2 symmetrical and asymmetrical stretching vibrations of PP and COC are assigned at 2869 and 2924 cm^{-1}respectively. CH_2 symmetrical and asymmetrical stretching vibration intensities of neat COC is higher than that of neat PP which is due to the presence of ethylene units in COC. Moreover, these vibration intensities decrease progressively as COC content reduces in PP/COC blends. CH_3 group symmetrical and asymmetrical stretching vibrations of PP are observed at 2885 and 2953 cm^{-1}respectively. These vibration intensities gradually decrease as PP content reduces in PP/COC blends and completely disappear in neat COC Raman spectrum. In COC40, COC50 and COC60 blends, both PP and COC characteristics peaks are observed and the intensities of these peaks are approximately at a similar level. This uniqueness occurred in COC40, COC50 and COC60 blends may be due to the co-continuous behaviour of the components in the blends. In particular, PP/COC blends with optimised mechanical, thermal and barrier properties can be used as an effective packaging material.

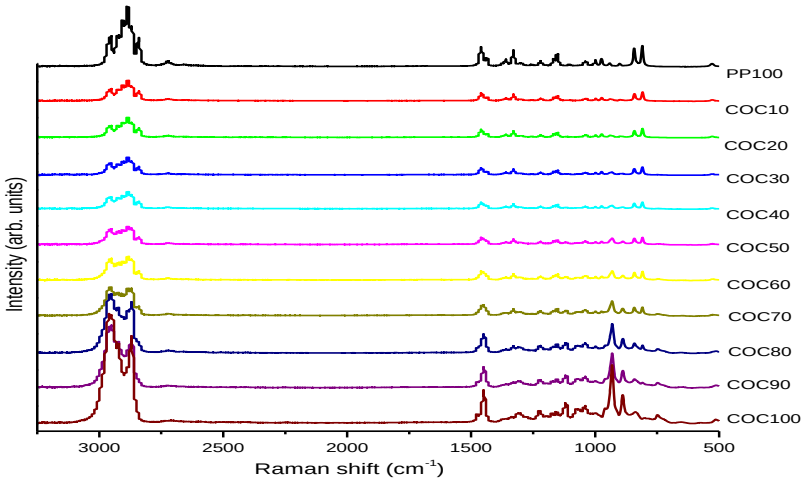


Figure 3: Raman spectra of the PP/COC blends

Measurement of PP/COC Blends Composition:

The assessment of the PP and COC content in the PP/COC blends is very significant during manufacturing and recycling applications. This evaluation can be achieved with Raman spectroscopy by measuring the peak intensity of fundamental vibrations of PP and COC. For this calculation, the peak at 932 and 1330 $cm^{-1}$for COC and PP respectively are selected as a fundamental reference band. The fundamental Raman peak of PP spectrum at 1330 cm^{-1}corresponds to the deformation mode of the C-H bond and twisting mode of the CH_2 groups [15]. The fundamental Raman peak of COC spectrum at 932 $cm^{-1}$is assigned to ring vibration mode of the norbornene units in CO. Table 3 shows the intensity of 932 and 1330 cm^{-1}bands and ratio of these fundamental Raman peak intensities. The ratio of the fundamental Raman peak intensities $[I_{932}/(I_{932}+I_{1330})]$ is useful to evaluate the PP and COC content in the PP/COC blends. Figure 4 shows the ratio of the fundamental intensities versus the COC content in weight percentage. It is observed that the considered data is very well matched with a linear dependence passing through the point (0, 0) and (100, 1). This technique helps to analyse the blend components of an unknown polymer material by using in a non-destructive way and quantitative information can be gathered for other applications [27].

Table 3: Intensity of fundamental Raman peak of COC, PP and ratio of the fundamental Raman peak intensities

Blend Composition (wt %)	**I_{932} (arb. units)**	**I_{1330} (arb. units)**	**I_{932} / (I_{932}+ I_{1330})**
COC100	1611	0	1.0
COC90	948	143	0.9
COC80	805	191	0.8
COC70	404	179	0.7
COC60	249	167	0.6
COC50	169	145	0.5
COC40	85	128	0.4
COC30	63	153	0.3
COC20	37	171	0.2
COC10	29	174	0.1
PP100	0	445	0.0

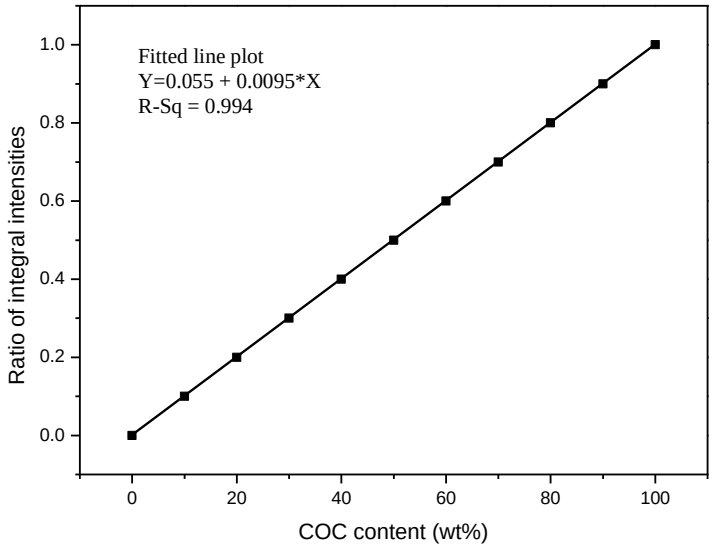


Figure 4: Ratio of the fundamental intensities versus the COC content in weight percentage

Conclusions:

PP/COC blends were prepared for entire composition range by varying the content of COC using co-rotating twin screw extruder. Raman spectroscopy investigations were effectively reported for the detailed study of the neat PP, neat COC, and PP/COC blends. The addition of COC to PP caused notable changes to the Raman spectrum of PP. It was established that difference in the contents of the blends led to considerable monotone variations in the PP/COC blends Raman spectra. The ratio of the integral intensities of the Raman bands allocated to the fundamental vibrations with frequencies of COC (932 cm^{-1}) and PP (1330 cm^{-1}) can be used for the quantitative study of COC and PP contents in the PP/COC blends. The evidence of both PP and COC

characteristics Raman vibrations and its resulting intensities in the COC40, COC50, and COC60 blends may be due to the co-continuity of the blend components.

Acknowledgement:

The authors are grateful to Dr. Wilfried Hatke (TOPAS Advanced Polymers, Germany) for providing cyclic olefin copolymers.

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