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Polyethylene oxide–fullerene nanocomposites

Nasar Ali

Dorina M. Chipara

Karen Lozano

James R. Hinthorne

Mircea Chipara

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Nasar Ali, Dorina Chipara[1], Karen Lozano[3], James Hinthorne[2], Mircea Chipara[2]

The NANOSMAT Society, Manchester, United Kingdom

[1]The University of Texas Rio Grande Valley, Department of Mechanical Engineering

Edinburg, TX 78539, USA

[3]The University of Texas Rio Grande Valley, Department of Physics, Edinburg, TX 78539, USA

 Highlights

- A new behavior of Raman spectra in polymer-fullerene nanocomposites is demonstrated.
- Effect of the nanofiller on the polymer/filler crystals are discussed
- Modifications on Raman lines due to the loading with C60 are reported.

ABSTRACT

Polyethylene oxide – fullerene nancomposites have been prepared by using the solution path with water as solvent (only for the polymer). The dispersion of C60 within the polymer solution was achieved by high power sonication. The study aims to a better understanding on the effect of C60 nanoparticles on the macromolecular chains. Raman and Wide Angle X Ray spectroscopy were used to inspect the interactions between nanofiller and macromolecular chains. The experimental results revealed a completely different behavior of fullerene dispersed within polymeric matrices than carbon nanotubes and nanofiller. The observed difference was assigned to the huge aspect ratio of carbon nanotubes and nanofibers (compared to the fullerene) and to the high thermal conductivity.

Keywords: fullerene; Raman; X-Ray; polyethylene oxide; nanocomposites

Introduction

Spherical fullerene C60, widely known as Buckminsterfullerenes, have been synthesized at Rice University by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto [1]. The C60 molecule has a Van der Waals diameter of about 1.1 nm and consists of 60 carbon atoms configured as a sphere (truncated icosahedron) built of 60 vertices and 32 faces (organized in12 pentagons and 20 hexagons[1], [2]). The C60 is characterized by two bonds lengths, one between the hexagons labelled as 6:6 ring and assigned as a double bond and the other between hexagons and heptagons, which is shorter than the double bond and is considered to be a single bond. The bonds have a dominant sp^2 hybridization, with a certain sp^3 admixture triggered by the local curvature may be noticed. In contrast with other nanostructures, C60 has a rather poor electrical conductivity and is soluble in some organic solvents [3]. However, C60 is not soluble in water [2]. Polyethylene oxide (PEO) is an intriguing polymer, with amphoteric features combining "hydrophobic ethylene units and the hydrophilic oxygens" [4]. Consequently, PEO is soluble both in water and in organic solvents. The polymer consists on C, H, and O atoms linked together into a linear chain and has a relatively high degree of crystallinity (about 50 %). The crystal of PEO has a monoclinic unit cell, consisting of seven units and two helical turns [4]per cell.

Experimental Methods

The fullerene (C60) has been purchased from CheapTubes and used as received. Polyethylene oxide with a molecular mass of 5,000,000 has been purchased from Sigma Aldrich. The PEO-C60 nanocomposites have been obtained by dispersing the PEO in water, at room temperature, addition of C60 nanoparticles to the homogeneous solution, and sonication of the mixture by using a high power sonicator (Hielscher), with a power of 1000 W for a period of 1 hour. The as obtained viscous solution was dried in an oven at 125 °C for 12 hours. Thermogravimmetric analysis (TGA) has been performed by using a TA instrument. Raman measurements have been performed by using a Renishaw InVia confocal microscope system equipped with a laser operating at 532 nm and a grating of 1800 lines/mm having a resolution of 2 cm^{-1}. Wide Angle X-Ray Scattering (WAXS) investigations have been performed by using a Discovery 8 Bruker spectrometer.

The Raman lines of the as prepared PEO-C60 nanocomposites including the pristine polymer (PEO) and the nanofiller (C60) are shown in Fig. 1.

Experimental Results and Discussions

Raman spectra of the C60 and of pristine PEO confirmed the structure and the purity (99% for C60)) of the as received chemicals. The spectra are included in Fig. 1 together with the Raman spectra of PEO-CNFs. TGA investigations of PEO-CNF nanocomposites confirmed the complete removal of water.

The far infrared region extends typically from 10 up to 400 cm^{-1} and is associated with low energy motions involving several atoms and molecules such as the linear acoustic mode (LAM) and the dynamic linear acoustic mode (DLAM) in polymers.

The nanofiller exhibits a strong line located at 273 cm^{-1}, with a weak shoulder at about 267 cm^{-1} (see Fig. 2) reflects the squashing of the H$_g$ mode [5]. This line disappears as the C60 is dispersed within the polymer and it is barely visible even for the nanocomposite containing 50 % wt. C60.

The weak line noticed at about 279 cm^{-1} in the pure and loaded PEO was assigned to the dynamical longitudinal acoustic mode. As expected the line is broad and weak. Upon the addition of fullerene, this line shifts gently towards lower wavenumbers and decays. This suggests that this vibration is weakened by the dispersion of C60 within the polymeric matrix. The conclusion, can be understood by observing that the Raman shift of the acoustic mode (in cm^{-1}) moves towards shorter wavenumbers as the mass of the oscillating group of molecules is increased. While this does not imply the inclusion of the nanofiller in the acoustic oscillation of the macromolecular chain, it demonstrates the interaction between the nanofiller and the polymeric matrix. A more detail quantitative analysis is difficult due to the overlap pf the lines located at 272 and 279 cm^{-1}. A weak line was noticed in pure PEO at 363 cm^{-1}. This line decays as the polymer is loaded by C60.

The skeletal region (see in Fig. 3 the Raman line in the domain 400 to 1200 cm^{-1}) extends typically from 400 to 1500 cm^{-1} and provides a fingerprint of the molecular vibrations occurring within the sample. Within this domain, Raman lines originating from C60 have been noticed at 433, 486, 496, 569, 711, 773, and 1101 cm^{-1}. The specific modes associated to these lines are included in Fig. 3. All these lines decay rapidly while the C60 is dispersed within the polymeric matrix. In contrast, in carbon nanotubes and nanofibers the Raman lines associated to the D and G modes have been reported even for composites containing less than 1 % wt. nanotubes. A relatively strong line, originating from C60) and assigned to the breathing Ag mode has been noticed at 496 cm^{-1}

[5]. The line decays rapidly in the nanocomposites reflecting the strong interaction with the polymeric network. Actually, this shows that the elastic matrix of the polymer is stretched to accommodate for the nanofiller. This generates a pressure upon the nanofiller than freezes the breathing mode.

In the skeletal region PEO shows lines at 845, 861, 1064, 1143, and 1395 cm^{-1}. The assignments for these lines are shown in Fig. 3. The Raman lines assigned to the polymeric matrices are decaying and broadening as the concentration of C60 is increased. However, no shifts have been noticed in the position of the Raman lines, within the experimental errors. Raman data indicate that the macromolecular chain is damping efficiently the vibration modes of C60, suggesting a weak interaction between the nanofiller and the polymer. From the decay of the PEO Raman lines in the skeletal region it is concluded that both the interactions between monomers (controlled by C-O-C modes) and eventually within the monomer (reflected by CH_2 rocking). However, the band located at 1255 cm^{-1} and assigned to amorphous or disordered chains [6]was not observed neither in pristine PEO nor in nanocomposites suggesting that the nanofiller did not generate important crystalline modifications.

The spectrum of C60 in the range 1440 to 1500 cm^{-1} consists of a strong line and a shoulder (see Fig. 4). These lines have a rather strong dependence on the loading of the matrix with PEO, with an overall weak displacement towards lower Raman shifts. The strongest component, centered at about 1469 cm^{-1}, was assigned to the Ag pentagonal pinch [5], reflecting tangential stretching. The weak shoulder, located at 1483 cm^{-1} may represent the Gg(6) mode [7]. , which typically is Raman forbidden although may be activated by a decrease of the local symmetry. The Raman line noticed at 1576 cm^{-1} is typical for insulating islands in C60 [8]. Upon the dispersing the C60 in the polymer, at high concentration of filler, the Raman shift is decreased suggesting a tendency towards conductive domains in C60 [8]. The polymeric matrix, exhibits also Raman lines at 1486 cm^{-1} assigned to CH_2 groups (in phase bending)[6].

For polymers, the Raman lines in the region 1500 to 2500 cm^{-1} are reflecting motions affecting double bonds involving a C atom (usually between 1500 and 2000 cm^{-1}) and triple bonds involving a C atom (between 2000 and 2500 cm^{-1}). As expected, the polymer does not exhibit any line in this range, as PEO does not include any double or triple bond. Nevertheless, the C60 showed a weak line at 1580 cm^{-1}, assigned to the C double bond, which may be speculated within the 6-6 carbon ring.

In the region 2500 to 4000 cm^{-1} there are no Raman lines originating from C60. However, the polymer exhibits in the region 2700 to 3000 cm^{-1} a complex overlap a Raman lines originating from O-H stretching (see Fig. 5). It is noticed that these modes are not significantly affected by the loading with C60, showing minor changes even for a loading with 50 % wt. C60.

Fig. 6 shows the WAXS spectra of PEO, C60, and of some nanocomposite. The peak at 19.2^o corresponds to [120] reflection and the peak at 23.3^o has been assigned by previous authors to different reflections ((032), (132), (112), (212), (004) or (124)). Fig. 7 provides a more detailed picture of the WAXS lines. It is noticed that the addition of fullerene shifts the lines originating from the polymeric matrix. Surprisingly, the shift is to larger 2theta values suggesting that the crystal is shrink by the polymeric matrix. It is speculated that the shift reflects the stress acting on the polymeric matrix due to the loading with C60.

Conclusions

Raman spectroscopy revealed a completely different behavior of the C60 filler compared to carbon nanotubes. Raman investigations on polymers doped with carbon nanotubes and nanofibers revealed a fast decay of the Raman lines associated to the polymeric matrix. Thus, the Raman spectrum of polymer-carbon nanotubes nanocomposites is dominated by the nanofiller spectrum, even at low concentrations of nanofiller. This has been reported in various polymers loaded with carbon nanotubes or nanofibers including PEO [9], isotactic polypropylene [10], polyvinylchloride [11]. This behavior was tentatively explained [10] by the high thermal conductivity and aspect ratio of carbon nanotubes and nanofibers, where local temperatures in the vicinity of the nanotube may be easily averaged out via the interactions between the polymeric chains and the nanofiller, where the nanofiller has a large thermal conductivity. The fullerene is missing the huge aspect ratio and hence can interact solely with the neighboring macromolecular chains, missing the opportunity to delocalize and average the local thermal spikes.

WAXS data revealed another interesting features. During the preparation of the nanocomposite, the polymer accommodated within its free volume some C60 nanoparticles. As a consequence the polymer was stretched and the size of the PEO crystallites decreased. This resulted in the broadening of the WAXs lines due to the polymer as well as in a slight shift towards larger 2 theta values. (consistent with smaller distances between crystalline planes).

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C 60: buckminsterfullerene, Nature. 318 (1985) 162. doi:10.1038/318162a0.

[2] W. Kratschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Solid C60: new form of carbon, Nature. 347 (1990) 354–358.

[3] R.M. R. S. Ruoff Doris S. Tse, D.C. Lorents, Solubility of C60 in a Variety of Solvents, J. Phys. Chem. 97 (1993) 3379–3383. doi:10.1021/j100115a049.

[4] F. Migliardo, S. Magazu, M.T. Caccamo, Infrared, Raman and INS studies of poly-ethylene oxide oligomers, J. Mol. Struct. 1048 (2013) 261–266. doi:10.1016/j.molstruc.2013.05.060.

[5] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden, H. Seki, et al., Vibrational Raman and infrared spectra of chromatographically separated C60 and C70 fullerene clusters, Chem. Phys. Lett. 179 (1991) 181–186. doi:10.1016/0009-2614(91)90312-W.

[6] I.S. Elashmawi, L. H. Gaabour, Raman, morphology and electrical behavior of nanocomposites based on PEO/PVDF with multi-walled carbon nanotubes, Results Phys. 5 (2015) 105–110. doi:10.1016/j.rinp.2015.04.005.

[7] S. Falke, P. Eravuchira, A. Materny, C. Lienau, Raman spectroscopic identification of fullerene inclusions in polymer/fullerene blends, J. Raman Spectrosc. 42 (2011) 1897–1900. doi:10.1002/jrs.2966.

[8] L.S. Grigoryan, H.D. Bist, S. Sathaiah, H. Clara, S. V. Sharma, N. Sudhakar, et al., Electron-molecular vibration interactions in undoped fullerene films. A micro-Raman study, Chem. Phys. Lett. 199 (1992) 360–364. doi:10.1016/0009-2614(92)80132-U.

[9] T. Chatterjee, K. Yurekli, V.G. Hadjiev, R. Krishnamoorti, Single-walled carbon nanotube dispersions in poly(ethylene oxide), Adv. Funct. Mater. 15 (2005) 1832–1838. doi:10.1002/adfm.200500290.

[10] M. Chipara, J.R. Villarreal, M.D. Chipara, K. Lozano, A.C. Chipara, D.J. Sellmyer, Spectroscopic investigations on polypropylene-carbon nanofiber composites. I. Raman and electron spin resonance spectroscopy, J. Polym. Sci. Part B Polym. Phys. 47 (2009) 1644–1652. doi:10.1002/polb.21766.

[11] M. Chipara, J. Cruz, E.R. Vega, J. Alarcon, T. Mion, D.M. Chipara, et al., Polyvinylchloride-single-walled carbon nanotube composites: Thermal and spectroscopic properties, J. Nanomater. 2012 (2012) 1–6. doi:10.1155/2012/435412.
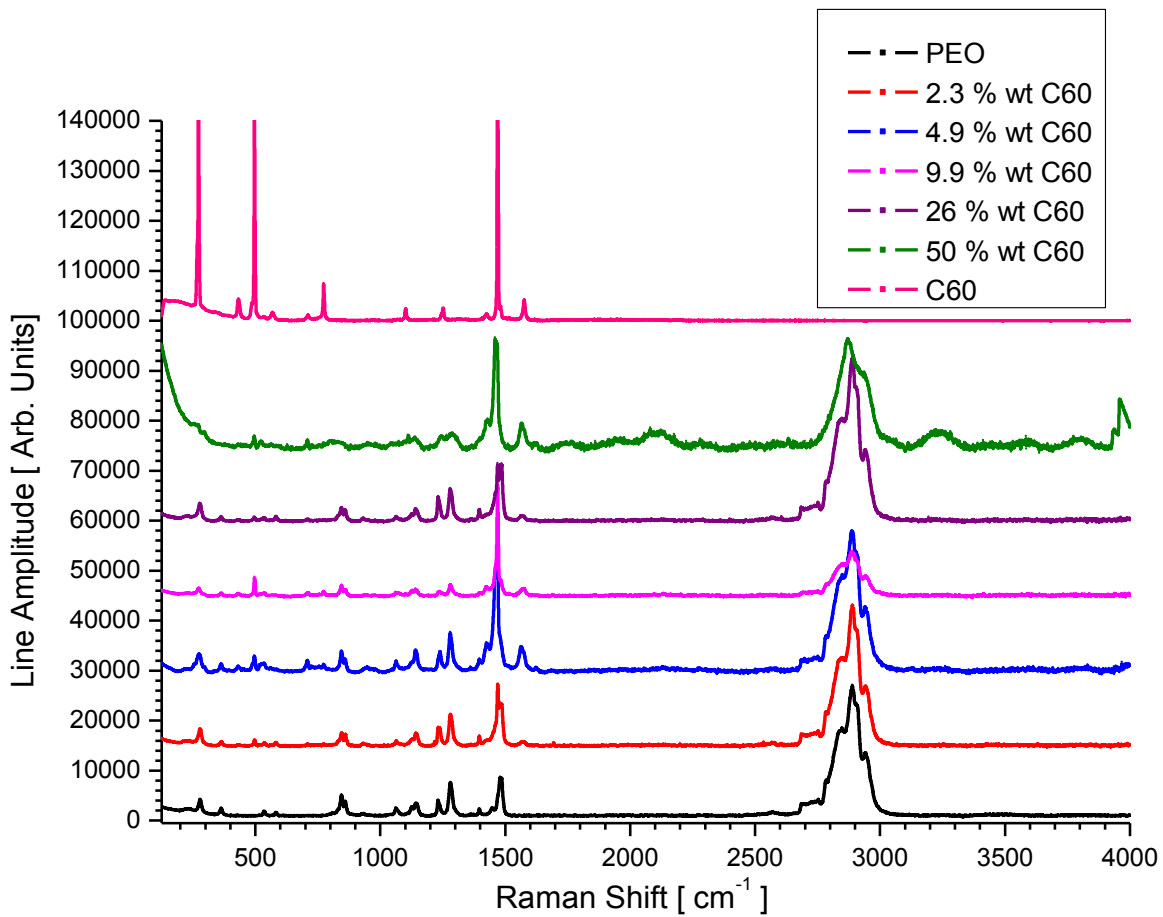
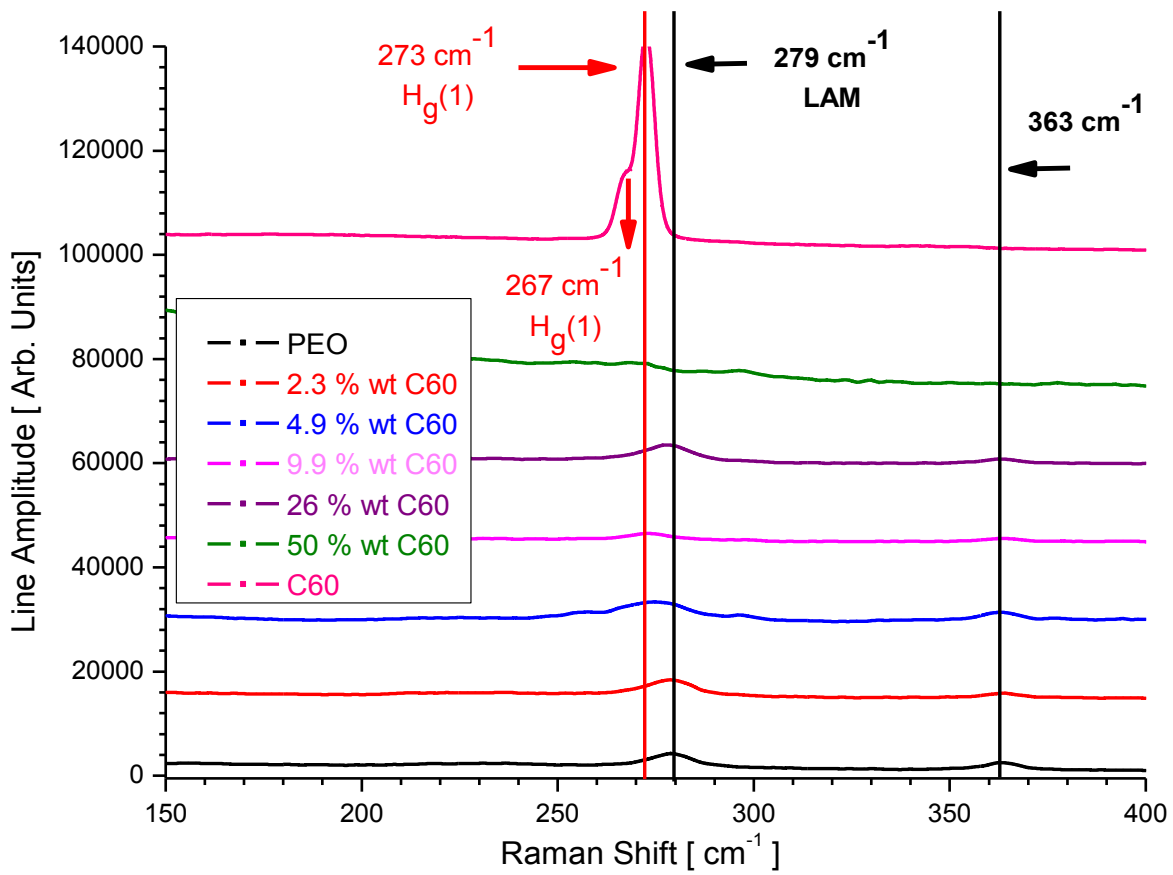Figure 1. Raman spectra of PEO, PEO-C60 nanocomposites and C60.

Figure 2. Raman spectra of PEO, PEO-C60 nanocomposites and C60 in the far infrared region.
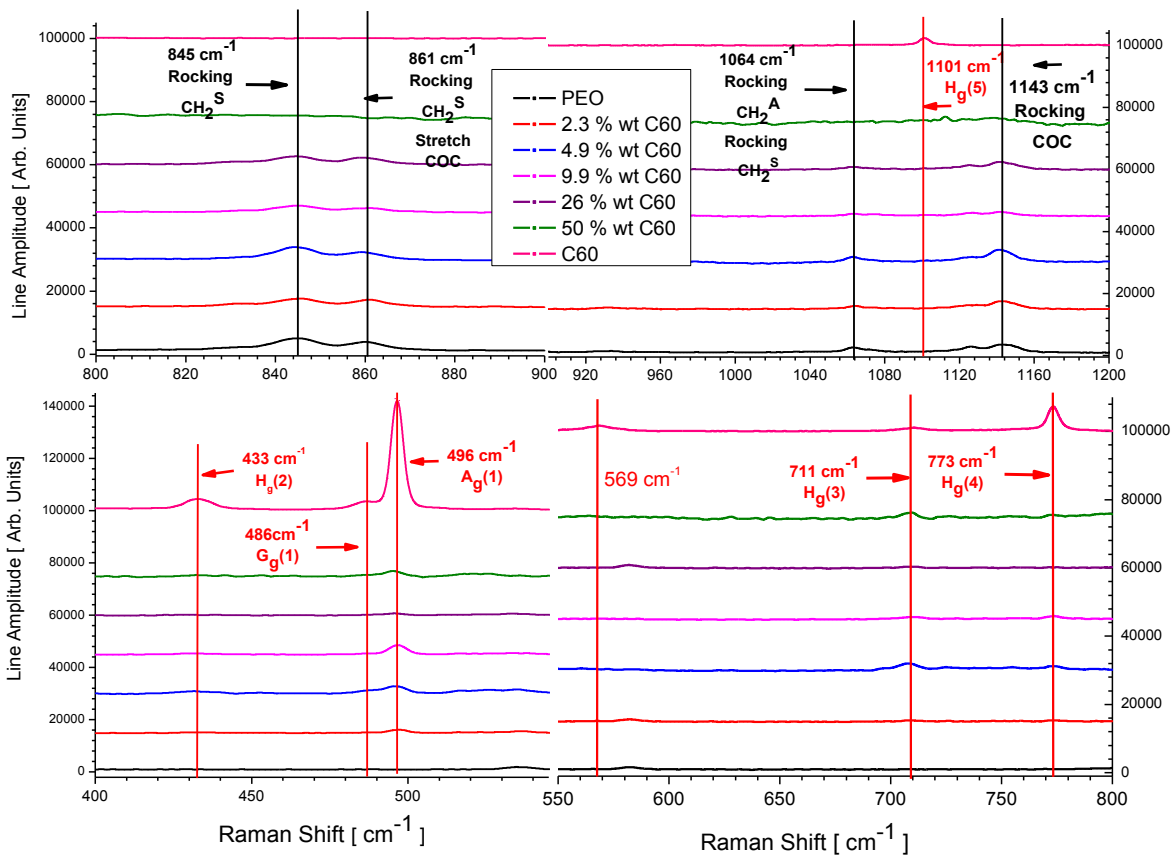
Figure 3. Raman spectra of PEO, PEO-C60 nanocomposites and C60 in the skeletal region.
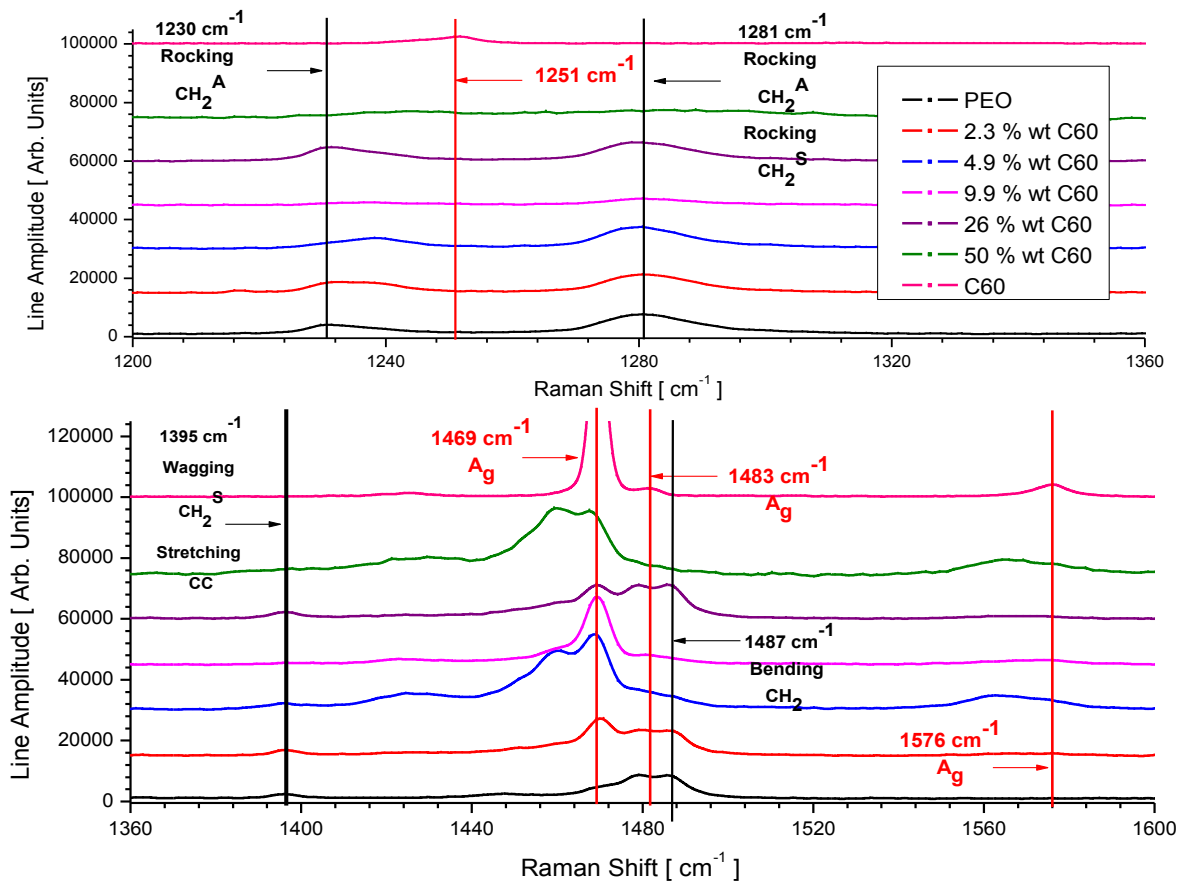
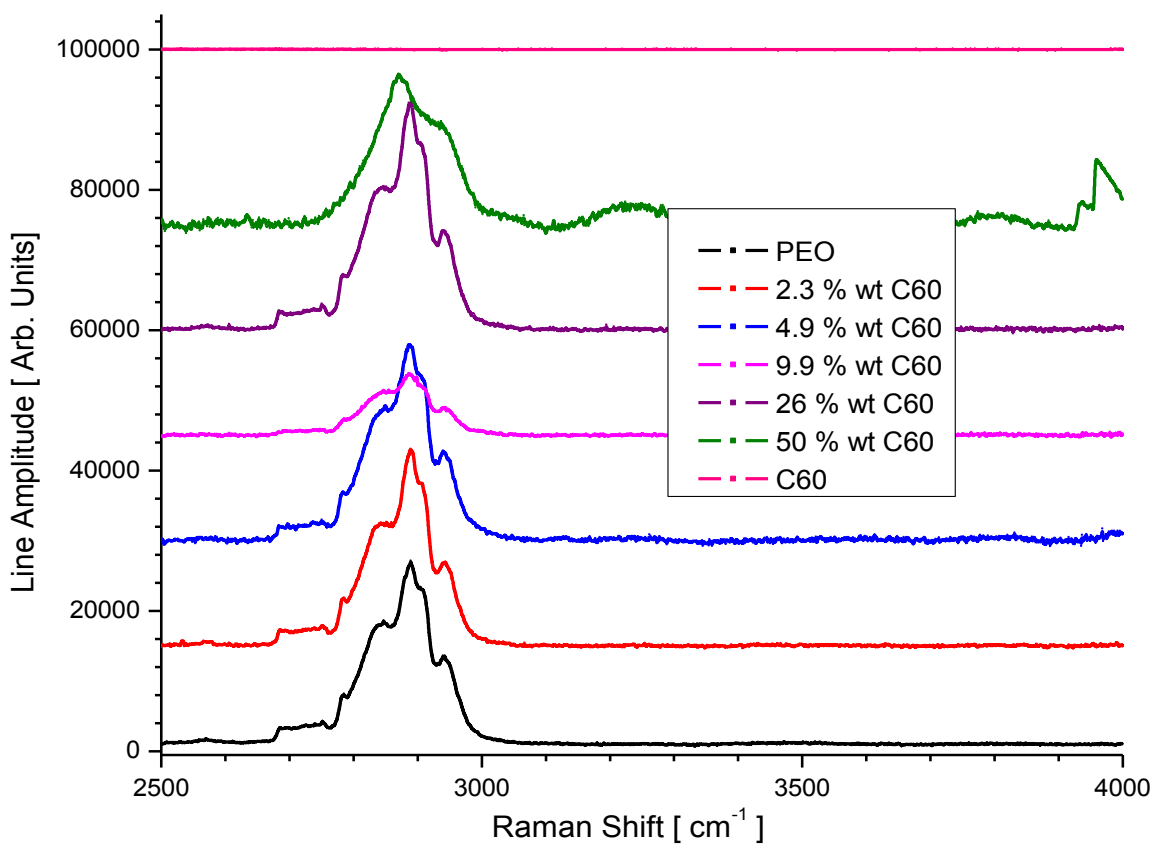Figure 4. Raman spectra of PEO, PEO-C60 nanocomposites and C60 in the region 1200 to 1600 cm^{-1}.

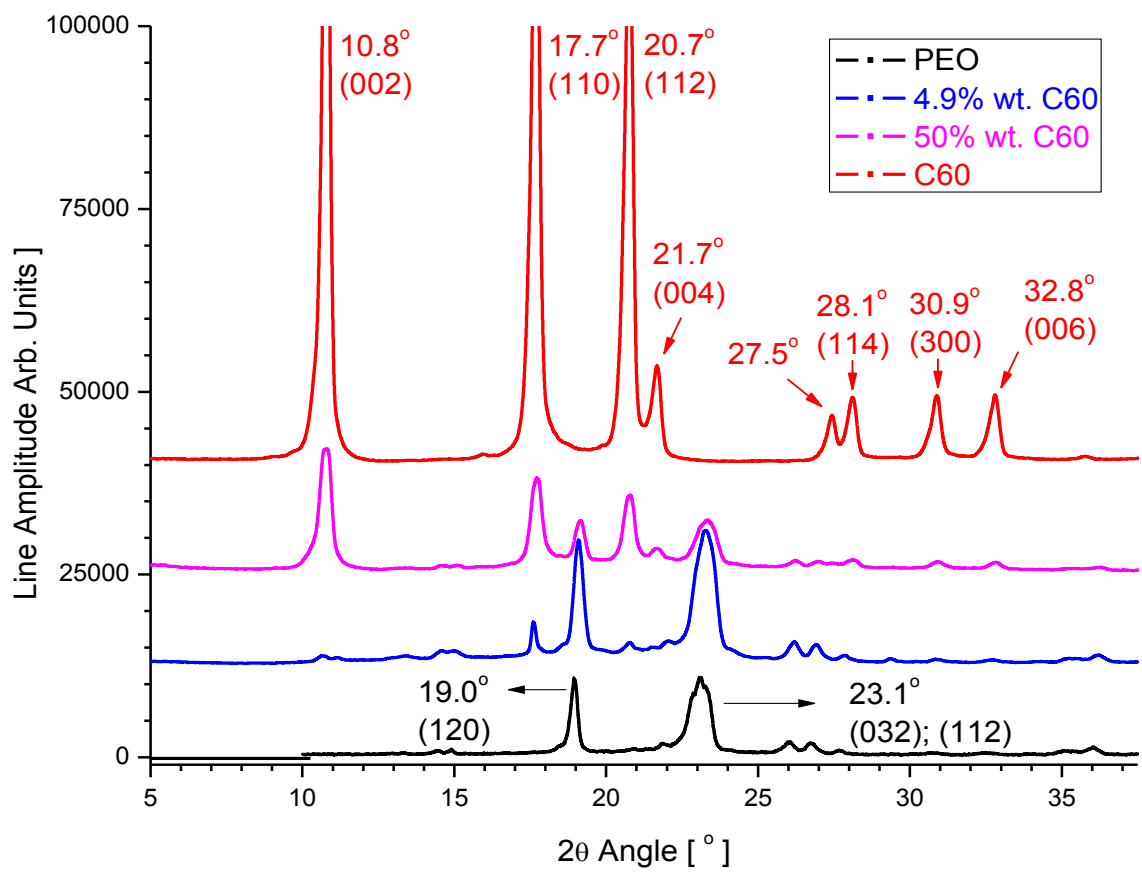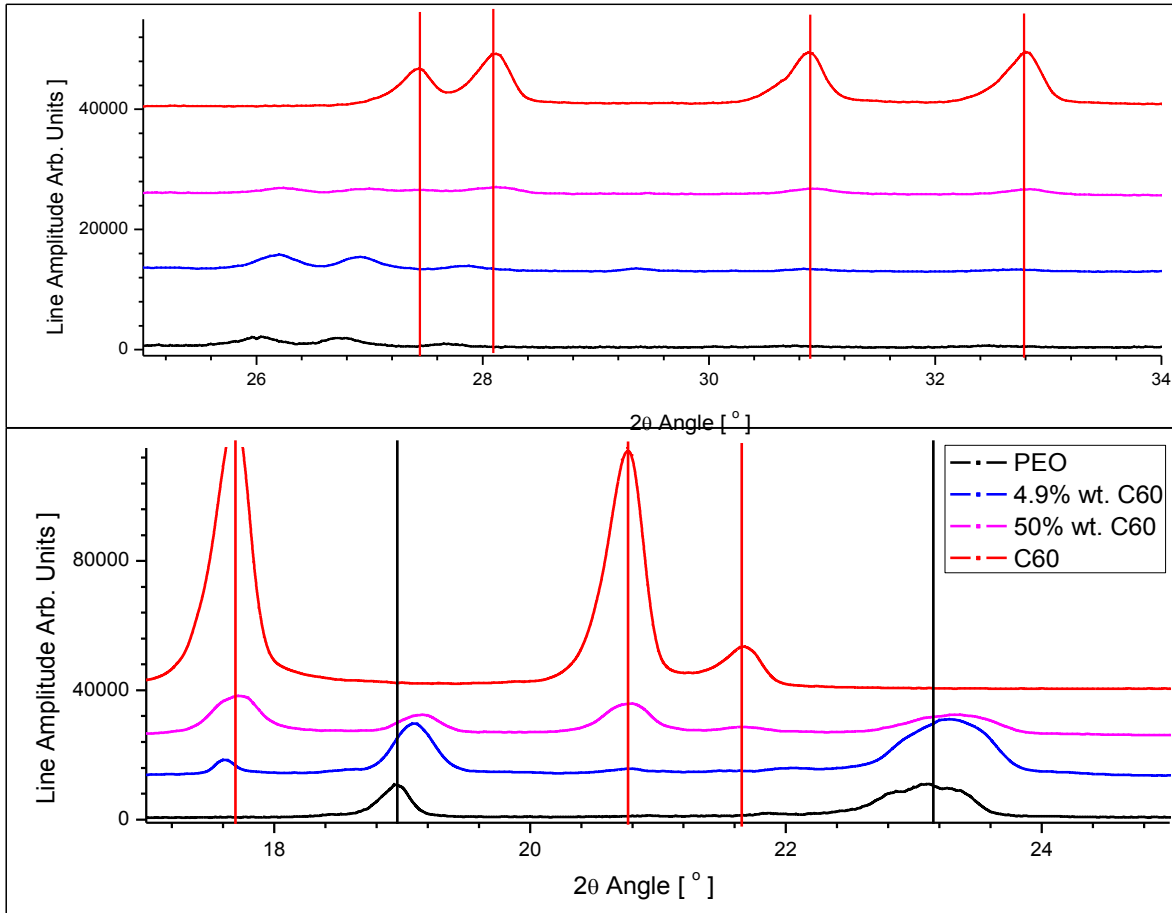Figure 5. Raman spectra of PEO, PEO-C60 nanocomposites and C60 in the 2500 to 4000 cm^{-1} region.

Figure 6. WAXS spectra of PEO, PEO-C60 nanocomposites and C60.

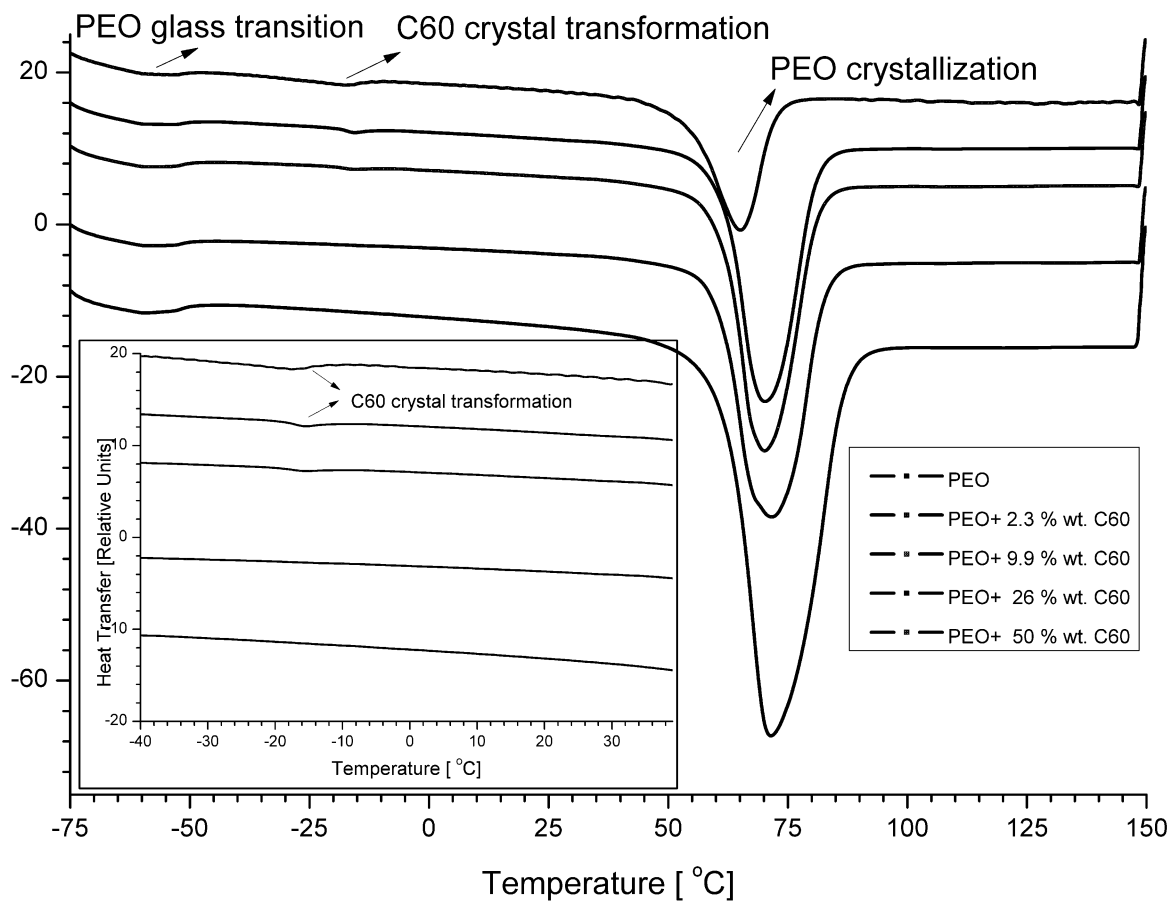Figure 7. Details of the WAXS spectra of PEO, PEO-C60 nanocomposites and C60.

Figure 8. DSC spectra of PEO and PEO-C60 nanocomposites showing from low temperatures to high temperatures the glass transition of PEO, the crystalline transformation of C60, and the melting temperature of PEO. The inset shows the crystallization of C60.
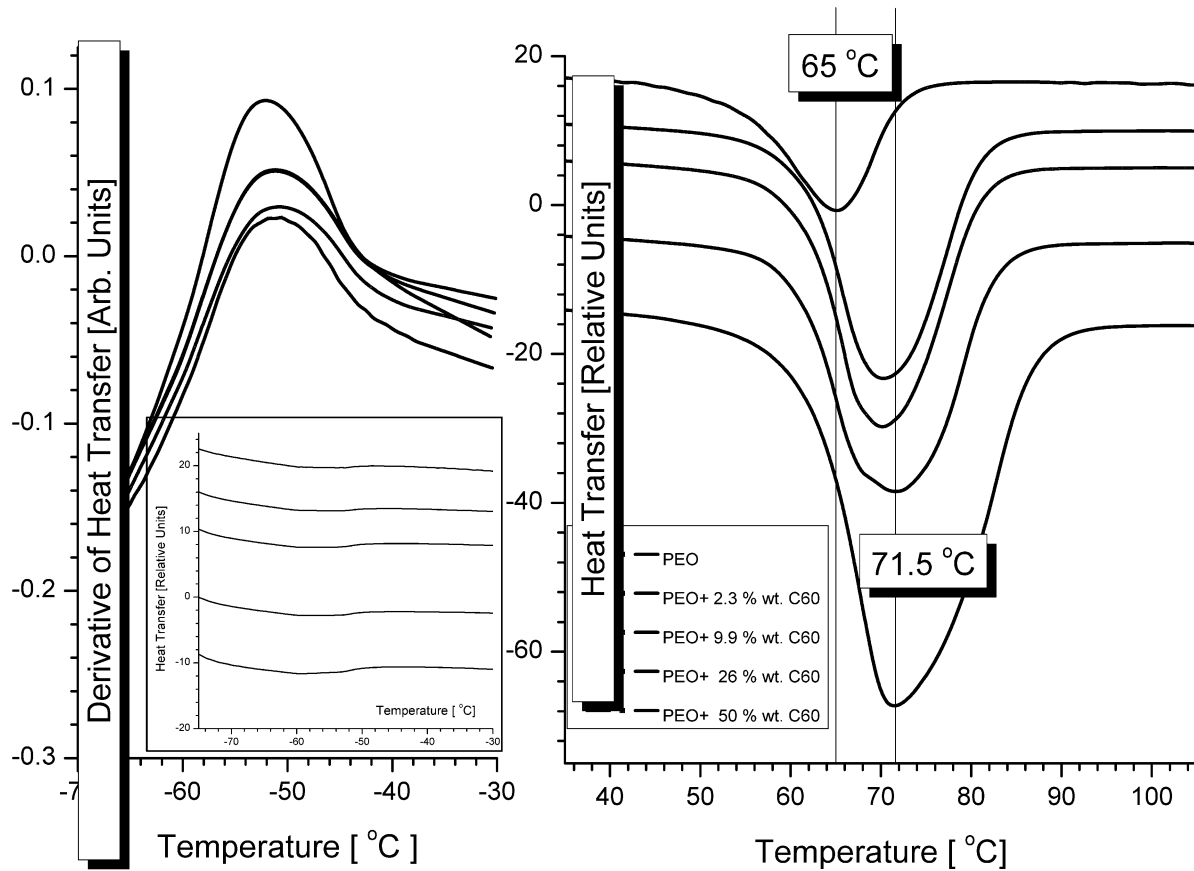
Figure 9. Left: The inset shows the glass transition temperature as measured by DSC while the left side figure shows the glass transition temperature as the extreme of the derivative of the heat transfer versus temperature. The peak position defines the glass transition temperature. Right side shows the crystallization in PEO and its nanocomposites.
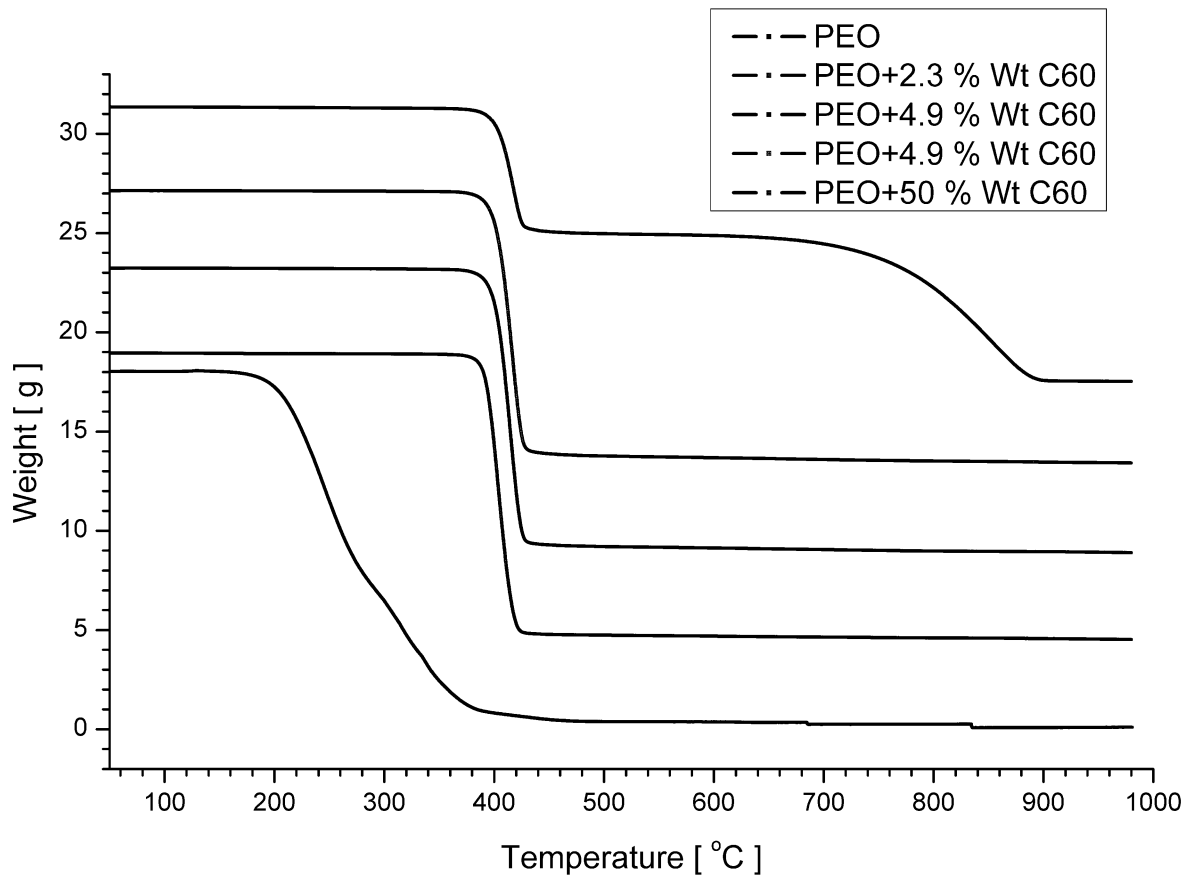
Figure 10. TGA data on PEO-C60 nanocomposites. Each thermogram was shifted upwards by 4 g for better visibility.