Raman Spectroscopy of Novel UHMW Polyethylene-Based Nanocomposites with Nanographite and Nanoclay

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Abstract. We analyze the Raman spectra of nanocomposites based on ultrahigh-molecular-weight polyethylene with nanoclay, thermoexpanded graphite, and reduced graphite oxide fillers. We discuss the potential of Raman spectroscopy for quantitative analysis of the nanocomposite structure, the influence of the fillers on the phase and conformation compositions of the polymer matrix, as well as for the monitoring of dispersion of the nanographite fillers in the nanocomposites.

1. Introduction

Modern industry requires state-of-the-art materials with a set of properties, which neat polymers (so-called homopolymers) in many cases cannot provide. For many applications, this problem can be solved by creation of polymeric blends, composites, and copolymers. For example, ultrahigh-molecular-weight polyethylene (UHMW PE), whose molecular weight \(M_w\) exceeds \(10^6\) Da, possesses the unique set of properties, such as chemical and temperature resistance, the friction coefficient, and physiological inertness [1, 2]. However, enhancement of important performance characteristics, such as stiffness, deformation, heat and wear resistances, is needed [1, 2]. For this reason, composites with UHMW PE matrix and different inorganic fillers are actively developed currently. Nanographite, graphene, and aluminum-silicate nanoclays are the promising fillers, which allow a significant modification of the polymer properties even at low filler content [1-4].

The structural diagnostics of such materials is of great importance, because the properties of any polymer composite material depend strongly on a numerous amount of structural characteristics (conformational and phase compositions of polymer matrix, filler content and sizes, polymer crystallite sizes, the degree of dispersion of a filler in a polymer matrix, etc.) [1-4].

Raman characterization of such objects most fully reveals the unique opportunities of this technique, allowing a nondestructive characterization of all the phases of semi-crystalline polymeric matrix, including non-crystalline areas, in which non-organic filler is localized. In particular, the relative content of crystallites (or the crystallinity degree) and the total content of \textit{trans}-conformers in PE and PE/clay nanocomposites can be evaluated by using the ratio of integral intensity \(I_{1415}^*\) of the PE Raman band at 1415 cm\(^{-1}\) and the reference intensity \(I_{1295}^*+I_{1305}^*\), that is the sum of integral intensities of the
PE bands at 1295 and 1305 cm\(^{-1}\) [5-9]. The band at 1415 cm\(^{-1}\) relates to the wagging vibrations of CH\(_2\) groups in PE macromolecules in the orthorhombic crystalline phase. The bands at 1295 and 1305 cm\(^{-1}\) are assigned to the twisting (\(\tau_{(CH_2)}\)) vibrations of CH\(_2\) groups [5-9]. The former belongs to the vibrations of \textit{trans}-conformers in PE macromolecules, which are localized in both the crystallites and the non-crystalline phase [5]. The latter is the vibrations of PE macromolecules with significant amount of \textit{gauche}-conformers in the non-crystalline phase [5]. The ratio of integral intensities I\(_I\)\textsubscript{1295}/I\(_I\)\textsubscript{ref} is a measure of the total content of \textit{trans}-conformers [5-9]. The depolarization ratio of the band at 1295 cm\(^{-1}\) gives information about orientational order of macromolecules in PE and PE-based nanocomposites [10, 11].

On the other hand, Raman spectroscopy is powerful technique for structural characterization of nanographite and graphene [12-17]. Analysis of the so-called G, D, 2D bands allows the monitoring of an amount of graphene layers and lateral sizes of graphite nanoflakes. The G band, corresponding to sp\(^2\) C=C bonds, is always active in Raman spectra of graphite materials [12-17]. The resonance-enhanced D band is due to structure defects in graphite materials [13-16]. For example, it is active in Raman spectra of micro- and nanographite, but it is not found in the spectrum of graphite monocrystal [14, 15]. The value of lateral size L\(_L\) of nanographite is inversely proportional to the ratio I\(_I\)\textsubscript{D}/I\(_I\)\textsubscript{G} of integral intensities of the D and G bands [13]. The shape and peak position of the resonance-enhanced 2D-band are reliable fingerprints to identify an amount of layers in graphite materials [17].

Currently, Raman spectroscopy is rarely used for structural study of PE nanocomposite with carbon and aluminum-silicate fillers, because of such composites are relatively novel materials. In particular, there are a few publications, concerning Raman characterization of PE/nanoclay composites [3, 9, 10]. Raman studies [2, 4, 18] of polymer nanocomposites with nanographite (or graphene) fillers are usually limited to structural characterization of the fillers.

In our contribution, we carry out Raman structural study of both polymer matrix and filler for UHMW PE nanocomposites with nanographite and nanoclay. Also, we consider the ways to take into account the contributions from the PE Raman bands, which can overlap with the Raman bands of nanographite. This analysis is required in order to extend the Raman methods of quantitative structural characterization to their applications to PE/graphite nanocomposites.

2. Experimental
We studied the films of the nanocomposites based on UHMW PE matrix (M\(_w\) = 2.0-2.5 \times 10\(^6\) Da) with three fillers: Cloisite 15A (MMT, Southern Clay Products, USA), thermoexpanded graphite (TEG), and reduced graphite oxide (RGO). The composites were synthesized by “\textit{in situ}” polymerization on the catalyst-activated filler surface [1]. The nanocomposite films with thickness of 0.5 mm were obtained via hot compression molding at 160°C and 10 MPa.

The nanocomposites UHMW PE/MMT, UHMW PE/TEG, and UHMW PE/RGO contain 5.3 and 8.3 wt\% of MMT, 1.6 and 7.8 wt\% of TEG, and 2.0 wt\% of RGO, respectively.

The MMT is an industrial Na\(^+\) montmorillonite clay, modified by alkylammonium salts, whose content was about 30 wt\%.

In order to produce the graphite nanoflakes (nanographite), the 50% aqueous ethanol solutions of TEG and RGO were treated via UV sonification (200 W, 10 min) with subsequent filtering and drying at 60°C in vacuum. In accordance with the X-ray diffraction studies [1], the thickness (L\(_{002}\)) of the graphite nanoflakes was 21 nm that is equal to 80-90 graphene layers. The scanning electron microscopy (SEM) data [1] displayed the lateral sizes of these nanoflakes from 1 to 10 nm.

To record Raman spectra of UHMW PE/MMT composites, we used a Sapphire SF 532 laser (Coherent Inc., USA), a double monochromator (U1000, Jobin Yvon, France) and Peltier-element cooled photomultiplier detector, operating in photon counting regime. The excitation wavelength was 532 nm. Spectra were recorded at 90°-scattering with the spectral resolution of 5 cm\(^{-1}\). Diameter of the laser spot on a sample was about 2 mm.

The Raman spectra of the UHMW PE/TEG and UHMW PE/RGO composites, as well as the TEG and graphite powders were recorded by Raman microscope spectrometer “Senterra” (Bruker, Germany).
The excitation wavelengths were 532 and 785 nm. The scattered light was collected in the backscattering geometry using a 20× lens (N.A.=0.65). The laser power at the sample and spectral resolution were 2 mW and 4 cm⁻¹, respectively.

Spectral analysis was performed by the homemade software, which provided the spectra deconvolution via a weighted sum of Gaussian and Lorentzian functions [19] for the PE bands and via Lorentzian fit for the G, D, 2D-bands of the carbon fillers. The baseline was described by a second-order polynomial and was fitted simultaneously with the Raman lines.

3. Results and Discussion

![Raman spectra](image)

**Figure 1.** Raman spectra (black) of UHMW PE/MMT composites with 8.3 and 5.3% of MMT contents and neat UHMW PE. The gray lines and open symbols are results of the deconvolution and the simulated spectrum, respectively.

Figure 1 shows the spectra of the neat UHMW PE and UHMW PE/MMT nanocomposites with 5.3 and 8.3 % of the filler contents. For the composite with 8.3 % of MMT, we also have plotted the results of the deconvolution analysis in the spectral region 1200-1550 cm⁻¹ as well as the simulated spectrum, which was obtained by summation of the spectral components, found by the deconvolution analysis, and the background.

Figure 2 shows the Raman spectra of the TEG, graphite powder and the UHMW PE film, recorded by using the excitation wavelength \( \lambda = 532 \) nm, the Raman spectrum of the graphite, recorded by using the wavelength \( \lambda = 785 \) nm as well as the results of the deconvolution analysis of the 2D band using two lines of Lorentzian/Gauss shapes.

In the spectra, which are plotted in Figures 1 and 2, the intensities in the regions 1200-1700 and 2450-3050 cm⁻¹ are normalized to the peak intensity of the bands at 1295 and 2881 cm⁻¹, respectively. Note, that the absolute peak intensity of the band at 2881 cm⁻¹ is approximately 4.5 times higher, than that of the band at 1295 cm⁻¹.
3.1. Raman characterization of PE-matrix

The separation of the contributions from the overlapping Raman bands of the fillers and PE-matrix is the main obstacle to quantify the structural characteristics of both the polymer matrix and filler by using Raman spectra.

Raman spectrum of MMT clay, modified by alkylammonium salts, contains the bands of the modifier at 1295 and 1305 cm\(^{-1}\) [20, 21]. However, the contributions of these bands to the integral intensities of \(\tau\) (CH\(_2\))-bands of PE are negligible [10], because the modifier content in polymer composites is usually low (< 3 wt%). Thus, we consider that Raman spectra of the UHMW PE/MMT composites in the regions 1200-1550 cm\(^{-1}\) are described by only the PE bands (Figure 1).

![Figure 1. Raman spectra of PE-matrix and fillers.](image)

Figure 2. Raman spectra (black) of the TEG, graphite and the neat UHMW PE, recorded at the 532 nm excitation, and Raman spectrum (black) of graphite, recorded at the 785 nm excitation. The gray lines and open symbols are results of the deconvolution analysis and the simulated spectrum, respectively.

We found out that the proper choice of the excitation wavelength allows to solve the problem of “overlapping bands” for PE composites with nanographite (or graphene) fillers. Namely, for the TEG and graphite powders under study the peak position of the D band was found at 1318 cm\(^{-1}\) at the excitation wavelength of 785 nm (Figure 2). At the 532 nm excitation the D band peak position is expected to shift to higher wavenumbers (Figure 2). It is observed at 1352 cm\(^{-1}\) for the TEG and graphite, and at 1350 cm\(^{-1}\) for the composites with the nanographite fillers (Figure 3). It is important to note that the D-band can be wide enough [14, 17]. For our samples at the 532 nm excitation the full width at the half-maximum (FWHM) of the D band was 40-48 cm\(^{-1}\) for the composites with the TEG filler and the TEG and graphite powders. FWHM of the D band reaches up 72 cm\(^{-1}\) for the nanocomposite with the RGO filler (Figure 3). In spite of such large width of the D band, the deconvolution in the spectral area 1200-1550 cm\(^{-1}\) allows to separate the PE components at 1295, 1305, and 1415 cm\(^{-1}\) (Figure 3). Thus, the crystallinity degree (\(\alpha_{cr}\)) and the total content of trans-conformers (\(\alpha_{trans}\)) of polymer matrix for the UHMW PE/MMT and UHMW PE/nanographite composites can be estimated from Raman spectra by the relations, suggested by G.R. Strobl and W. Hagedorn for neat PE [5]:

\[
\alpha_{cr} (%) = 100 \times \left( \frac{I*_{1415}}{kI*_{ref}} \right) \quad (1)
\]

\[
\alpha_{trans} (%) = 100 \times \left( \frac{I*_{1295}}{I*_{ref}} \right) \quad (2)
\]

Here, the normalization coefficient \(k=0.43\) was calculated from the Raman spectra of solid n-alkanes with the degree of crystallinity of 100% (recorded at the same conditions as the spectra of the neat UHMW PE and the composites).
Table 1 contains the values of $\alpha_c$ and $\alpha_{\text{trans}}$, which were calculated by using the formulas (1) and (2) for the neat UHMW PE and the nanocomposites under study. Also, Table 1 presents the ratio $I_{2848}/I_{2881}$ of the peak intensities of the bands at 2848 and 2881 cm$^{-1}$ (the symmetric and asymmetric stretching vibrations of CH$_2$ groups, respectively), which decreases at growth of $\alpha_{\text{trans}}$ [22].

### Table 1. The degree of crystallinity $\alpha_c$, the total content of trans-conformers $\alpha_{\text{trans}}$, and the ratio $I_{2848}/I_{2881}$, calculated for the neat UHMW PE and for the polymer matrix of the nanocomposites.

| Filler content, wt% | $\alpha_c$, % | $\alpha_{\text{trans}}$, % | $I_{2848}/I_{2881}$ |
|---------------------|--------------|-----------------|-----------------|
| UHMW PE/MMT composites | 5.3          | 38              | 52              | 0.81           |
|                     | 8.3          | 40              | 62              | 0.68           |
| UHMW PE/TEG composites | 1.6          | 40              | 58              | 0.73           |
|                     | 7.8          | 53              | 67              | 0.70           |
| UHMW PE/RGO composite | 2.0          | 41              | 43              | 0.81           |
|                     | 0            | 40              | 54              | 0.79           |
| Neat UHMW PE         |              |                 |                 |                |

The amount of trans-conformers in the non-crystalline phase can be estimated as the difference between $\alpha_{\text{trans}}$ and $\alpha_c$ [5]. The value (100 % - $\alpha_{\text{trans}}$) can be used as a measure of the content of gauche conformers [5].

It can be seen from Table 1 that the non-crystalline phase of the neat UHMW PE and the nanocomposites under study contains mostly PE macromolecules with a numerous content of gauche conformers. However, the introduction of the fillers can slightly increase the content of trans-conformers in this phase.

#### 3.2. Raman characterization of the nanographite fillers

Figure 3 shows Raman spectra of the UHMW PE/RGO composite with RGO content of 2.0 %, the UHMW PE/TEG composites with TEG contents of 1.6 and 7.8 %, the neat UHMW PE as well as the results of the deconvolution analysis of these spectra in the areas 1200-1550 and 2600-2800 cm$^{-1}$. The intensities of the bands in the Raman spectra in Figure 3 are normalized to the peak intensity of the G band.

The G band in the spectra of the graphite is observed at 1583 and 1580 cm$^{-1}$ at the excitation wavelengths of 532 and 785 nm, respectively (Figure 2). Also, in the spectra, recorded at $\lambda = 532$ nm, this band is found at 1581 and 1579 cm$^{-1}$ for the UHMW PE/RGO and UHMW PE/TEG composites, respectively (Figure 3). Such shifts of the G band are comparable with the value of the spectral resolution used. However, we observed these shifts for all the spectra recorded at different points of the samples. This result demonstrates that the peak position of the G band is sensitive to both an excitation wavelength and kind of graphitic material. The similar result was observed early for various graphitic materials [14].

We observed the D band for the nanocomposites with 2.0 % of RGO and 7.8 % of TEG filler, but we could not recognize this band in the spectrum of nanocomposite with 1.6 % of TEG filler.

In accordance with the study [13], the lateral size $L_a$ of nanographite plates can be estimated by using the formula:

$$L_a (\text{nm}) = 2.4 \times 10^{10} \times \lambda^3 \times (I^*_{D}/I^*_{G})^{-1}$$  \hspace{1cm} (3)

Here, $\lambda$ (nm) is the excitation wavelength.
Figure 3. Raman spectra (black) of the UHMW PE/RGO composite with 2.0 % of RGO, the UHMW PE/TEG composites with 1.6 and 7.8 % of TEG, and the neat UHMW PE. The gray lines are results of the deconvolution analysis and the simulated spectrum.

We used the formula (3) and the Raman spectra, recorded at the 532 nm excitation, to evaluate the size $L_a$ for the PE/nanographite composites. We applied two methods of calculations. In the first approach we neglected the contribution from the weak PE band at 1368 cm$^{-1}$ in the intensity $I^*_D$. In the second approach we took into account the contribution of the PE band at 1368 cm$^{-1}$ as $0.1\times I^*_\text{ref}$, which was subtracted from $I^*_D$. The value $0.1\times I^*_\text{ref}$ is the integral intensity of the PE band at 1368 cm$^{-1}$, which was calculated by using the Raman spectrum of the neat UHMW PE and was expressed as proportion of the reference intensity $I^*_\text{ref}$. The two values calculated by different ways coincided within the range of measurement error.

We estimated the size $L_a$ as 10-11 and 38-40 nm for the UHMW PE/RGO composites with 2.0 % of the filler and for the UHMW PE/TEG composites with 7.8 % of the filler, respectively. Note that these values are much less than the lateral sizes (1-10 μm), which were detected by the SEM study [1]. This fact is explained by different sensitivity of Raman and SEM techniques. In particular, Raman spectroscopy is not effective for evaluation of large lateral sizes (1 μm and more) of particles of graphite materials [14, 15]. Thus, the absence of the D band in the spectrum of the PE/TEG composite with 1.6 % of filler can be a result of relatively large lateral size $L_a$ of filler crystallites.

Note that overlapping of the D and $\tau$ (CH$_2$) bands does not allow to use the excitation wavelength of 785 nm for evaluation of the size $L_a$ of the filler. However, this excitation wavelength is favourable to identify the dispersion degree of filler in PE matrix. At the 785 nm excitation we found out that the 2D band is observed at wavenumber of 2563 cm$^{-1}$, and it does not overlap with the Raman bands of PE. Unfortunately, the low sensitivity of our spectrometer in IR region did not allow us to record the spectra for the wavenumbers upper than 2740 cm$^{-1}$. 
At the excitation wavelength of 532 nm the 2D band in the Raman spectra of the graphite, TEG, and all the composites under study is of complex shape, which can be described by two contributions that are so – called $2D_1$ and $2D_2$ components [17]. The $2D_1$ component is found at 2683, 2686, and 2688 cm$^{-1}$ for the graphite, the TEG and the composites, respectively. The component $2D_2$ has the peak positions at 2715 cm$^{-1}$ for the UHMW PE/RGO composite, at 2721 cm$^{-1}$ for the graphite, and at 2722 cm$^{-1}$ for the TEG and the UHMW PE/TEG composites.

Decrease in an amount of graphene layers results in growth of intensity of the $2D_1$ component and an increment enhancement of the $2D_2$ component as well as in decrease in the ratio $I_{2D}/I_G$ of intensities of the 2D band and the G band [17]. The intensity of the 2D band is determined as the maximum intensity without spectrum deconvolution. The 2D band splitting vanishes in the Raman spectra of graphene. For instance [17], at the 514.5 nm excitation the Raman spectrum of graphene demonstrates the single 2D band with the peak position at 2688 cm$^{-1}$ and the ratio $I_{2D}/I_G = 5$, while the Raman spectrum of the bilayer structure contains the $2D_1$ and $2D_2$ bands with almost equal intensities and the ratio $I_{2D}/I_G = 2.5$.

However, the Raman spectrum of the neat PE contains a weak band at 2724 cm$^{-1}$, whose contribution should be taken into account at an analysis of the filler dispersion in the polymer matrix.

For the samples under this study, the values of the ratio $I_{2D}/I_G$ were estimated to be 0.43-0.46 for the graphite, the TEG, and the UHMW PE/RGO composite, while this ratio for the UHMW PE/TEG composites was equal to 0.77 and 0.82 for 1.6 and 7.8 % of filler contents, respectively. For the neat UHMW PE we found out that the peak intensity of the PE Raman band at 2724 cm$^{-1}$ is about 20 % from that of the PE Raman band at 1295 cm$^{-1}$. In turn, the peak intensity of the PE band at 1295 cm$^{-1}$ in the Raman spectra of all the composites under study is about 50 % from the peak intensity of the G band.

In other words, for the investigated composites the contribution of intensity of the PE band at 2724 cm$^{-1}$ to the peak intensity at about 2722 cm$^{-1}$ is estimated to be about 10 % from the peak intensity of the G band (we consider that $I_G = 1$). Thus, the observed shift of the $2D_1$ component, the increase in the ratio $I_{2D}/I_G$ in the spectra of the UHMW PE/TEG composites in comparison with the spectrum of the neat TEG is due to the increase in the dispersion degree of the TEG nanoplates in polymer matrix.

However, reliable Raman analysis in the spectral region 2600-2800 cm$^{-1}$ for the UHMW PE/RGO composite needs an additional studies, because of the contradiction between the two experimental observations: the almost equal intensities of the $2D_1$ and $2D_2$ components (indicating presence of the graphene bilayer) and the low intensity ratio $I_{2D}/I_G = 0.43$ (indicating presence of graphite). We consider that this effect is due to a noticeable contribution of the PE band at 2724 cm$^{-1}$ to the intensity of the $2D_2$ component.

4. Conclusions
In this study we analyzed the Raman spectra of nanocomposites of ultrahigh molecular weight polyethylene (UHMW PE) and nanoclay and two grades of UHMW PE/nanographite nanocomposites – with thermoexpanded graphite (TEG) and reduced graphite oxide (RGO) fillers.

Our main conclusions are:
1. The Raman method [5], elaborated for quantitative characterization of the phase and conformational compositions of neat polyethylene (PE), can be applied without any modification to an analysis of the same characteristics of PE matrix in nanocomposites with nanoclays or nanographite fillers. It is important to note that in this case spectra of the PE/nanographite composites should be recorded at the excitation wavelength of 532 nm. The applicability of this method [5] for analysis of Raman spectra recorded at other excitation wavelengths is required an additional study, because of overlapping of Raman bands of PE and nanographite.
2. At the excitation wavelength of 532 nm the Raman method [13], elaborated for an estimation of the lateral sizes of nanographite particles, can be extended to PE/nanographite composites without any modification.
3. The analysis of the 2D band in the composite Raman spectra, recorded at the excitation wavelength of 532 nm, allows qualitative characterization of the dispersion degree of the filler in PE/nanographite...
composites. However, the excitation wavelength of 785 nm is more preferable for evaluation of the dispersion degree, because of absence of overlapping of the 2D band of the filler and the PE bands.

4. For the UHMW PE/nanoclay and UHMW PE/nanographite composites under study we found that their non-crystalline areas contain mostly PE macromolecules with a numerous content of gauche conformers. At the same time, introduction of the fillers can slightly increase the content of trans-conformers in these areas.

5. We found out that the TEG nanoplates in the polymer matrix consist of a smaller amount of graphene layers in comparison with the source TEG.

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