QUANTIFICATION OF DISPERSION AND MIXING OF NANOFILLERS IN POLYETHYLENE COMPOSITES USING RAMAN SPECTROSCOPY

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ABSTRACT

A simple technique to quantify the dispersion, distribution and mixing of nanofillers in thermoplastic is required. This paper reports the use of vibrational spectroscopy for this purpose. The combination of Raman images and chemical images is used to quantify the dispersion, distribution and mixing of cellulose nanocrystal (CNCs) and multiwalled nanotube (MWCNTs) in high density polyethylene (HDPE) matrix composites. In addition to this the use of poly(ethylene oxide) (PEO) as a compatibiliser for the CNCs is investigated. Spatially resolved confocal Raman microscopy images reveal the distribution of the fillers in the HDPE matrix, while chemical images show the degree of mixing between the fillers and matrix. The method is shown to be equally useful for studying both nanofillers with a lower and higher degree of mixing; namely for CNCs and MWCNTs respectively. The sensitivity of the spectroscopic technique for evaluating chemical compositions of composites provides an additional information about the various stages of the production process.

1 INTRODUCTION

Polymer-based composites have attracted growing interest in recent years. Research has focused on the simplification of production methods, in order to make them realistic at a larger scale. Thermoplastic matrices are considered to be the future for large volume production of composites since they are potentially re-moldable, are low cost and can be formed using mature technology (extrusion, injection molding etc.). The enhancement of the mechanical properties thermoplastic composites can be achieved with the incorporation of nanofillers. Nanofillers such as, cellulose nanocrystals (CNCs) and carbon nanotubes (CNTs), are known to have high mechanical properties (stiffness, strength) and also high surface to volume ratios. This latter property means they possess a large surface area which is exposed for interactions with the matrix, when they are dispersed into their nanometer scale dimensions. The enhanced properties of composites are achievable when the production method enables good mixing and/or dispersion of fillers in the matrix and therefore strong interfacial adhesion between both phases. In the case of CNCs, casting/evaporation methods have exhibited good dispersions in organic solvents, and subsequently into thermoplastic materials. However, this approach is non-scalable on an industrial level [1, 2]. Alternatively, the use of a powdered compatibilizer is scalable for industrial melt compounding. Compatibilizers such as maleic anhydride grafted polyethylene (MAPE) [3] and poly(ethylene oxide) (PEO) [4] have been used to improve chemical compatibility between CNCs and polyethylene.

Improvements in the optics for vibrational spectroscopy methods such as Raman and IR has opened opportunities to study composite materials [5-7]. Unlike traditional methods, spectroscopic imaging is able to quantify the degree of mixing and the interface between thermoplastics and nanofillers. Furthermore, it provides detailed structural and molecular information on composite structure and
mophologies. This results from the combination of the structural and chemical ‘fingerprint’ of the spectroscopic analysis with the visualization of optical microscopy.

In this paper Raman imaging and chemical imaging are used to quantify the dispersion and the degree of mixing of CNCs-PEO-HDPE and MWCNTs-HDPE nanocomposites. The qualitative-quantitative analysis of the Raman images provides an assessment on the composites’ mechanical properties.

2 EXPERIMENTAL

Freeze-dried cellulose nanocrystals were prepared by acid hydrolysis from Whatman No. 1 filter paper as a source of cotton cellulose following the procedure described previously by Sapkota et al. [8]. Multiwalled carbon nanotube (MWCNTs) fillers were purchased from Arkema and used as a master batch; 25% in weight of MWCNT dispersed in high-density polyethylene (Graphistrength C HDPE1-25). High density polyethylene (Arboblend HDPE) with a molecular weight of \( M_w = 1.33 \times 10^5 \text{ g/mol} \) was supplied by Tecnaro GmbH, while poly(ethylene oxide) (PEO) with a molecular weight of \( M_w = 5 \times 10^6 \text{ g/mol} \) was provided by Sigma Aldrich (Dorset, UK). A master batch of CNCs-PEO was prepared before the fabrication of composites. PEO was dissolved into distilled water (1.25 wt%) and weakly stirred at 500 rpm at room temperature for 4 days. During that time, the vessel was covered to avoid photo-oxidation of PEO. Subsequently, an aqueous suspension of CNCs was added to the PEO vessel (50:50 PEO:dry content of CNCs, amount based on PEO amount). Then, distilled water was added to ensure the resulting suspension of PEO/CNCs has an overall PEO concentration of 1 wt%. These suspensions were then freeze dried before melt compounding. All HDPE composites were prepared by melt-compounding in a counter rotating twin-screw extruder (HAAKE Rheomex CTW5, Thermo Fisher Scientific). Composites containing CNCs as nanofillers were extruded at a temperature of 160 °C. The mixing speed was 70 rpm for 7 min to allow the non-cellulosic components to melt. Prior to extrusion, the CNCs-PEO master batch and matrix were blended in a mortar for 8 minutes. The mixture was dried in a vacuum oven at a temperature of 60°C for 24h to remove humidity. Composites containing MWCNTs as nanofillers were extruded at a temperature of 210 °C. The mixing speed was 50 rpm for 10 min. Prior to extrusion the pellets of the master batch of MWCNTs and HDPE were mixed.

Raman images were collected using a confocal Raman microscope, Alpha300 (WITec) equipped with a thermoelectrically cooled CCD detector (down to –61 °C). A 532 nm wavelength laser was used to accumulate high resolution Raman images from cross-sections of composite filaments. The laser power was adjusted to ~13 mW for the mapping of the CNCs-PEO-HDPE composites, while it was reduced to ~2.3 mW for MWCNTs-HDPE composites to minimize heating and melting of the samples. A 50× objective lens was used for backscattered light collection. The spectrometer grating was 600 g/mm (grooves/millimeter). Raman images were recorded over an area of 50x50 µm^2 with a step size of 0.2 µm. An exposure time per spectrum of 0.2 s for the CNCs-PEO-HDPE composites and 0.1 s for MWCNTs-HDPE composites was used. A total of 62500 Raman spectra were obtained for each map. The average number of maps per composite was two. A 785 nm wavelength laser was used to accumulate large area Raman images from cross-sections of CNCs-PEO-HDPE composite filaments. A 50x objective lens was also used for the collection of the backscattered light. The spectrometer grating was 600 g/mm (grooves/millimeter). Raman images were recorded over an area of 200x200 µm^2 with a step size of 2.0 µm. The exposure time per spectrum was 4 s. A total of 10000 Raman spectra were obtained for each map. The average number of maps per composite was two. WITec Project Plus software was used to analyze Raman images and to convert them into chemical images.

3 RESULTS AND DISCUSSION

3.1 Cellulose nanocrystals as fillers

Raman imaging of CNCs containing composites provides information on the spatial distribution of each component in the image. Each of these components has a unique structural and chemical
“fingerprint” distinguishable by spectroscopic analysis using characteristic Raman bands. A narrow Raman band located at ~1296 cm$^{-1}$ corresponding to -CH$_2$ twisting modes is utilized for differentiation of the HDPE matrix from CNCs [9, 10]. An additional Raman band centered at ~1441 cm$^{-1}$, assigned to a -CH$_2$ bending mode, is used to distinguish the HDPE matrix from the PEO compatibilizer. The Raman bands located at ~1281 cm$^{-1}$ and ~1482 cm$^{-1}$ corresponding respectively to, -CH$_2$ torsion modes and -CH$_2$ bending modes, typical for PEO compatibilizer are used to differentiate this material from both HDPE and CNCs [11]. The presence of CNCs in the Raman images is verified by the Raman band located at ~1098 cm$^{-1}$, corresponding to the C–O ring stretching modes and the β-1,4 glycosidic linkage (C–O–C) stretching modes between the glucose rings of the cellulose chains [12, 13]. Additionally a number of other Raman bands in the range of 250-600 cm$^{-1}$ corresponding to C-C, C-O-C, O-C-C, O-C-O skeletal-bending modes are distinctive for cellulose (and CNCs).

Figure 1 presents Raman images of a typical cross-section of a 2.50% CNCs-PEO-HDPE composite filament. The intensity of the colour in the Raman images reflects the intensity of selected Raman bands. For both images, a bright yellow colour indicates the highest intensity of the selected Raman band, while a dark brown colour shows the absence or significantly low intensity of the same band. Figure 1A displays the intensity of the Raman band located at ~1098 cm$^{-1}$, characteristic for CNCs. The concentration of the yellow area in the center of the image suggests a higher density of CNCs in that area. This aggregate of CNCs has an irregular shape and exhibits a variation in the intensity of the yellow colour. The Raman image corresponding to the Raman band located at ~1296 cm$^{-1}$, characteristic of the HDPE matrix, is shown in Figure 1B. This image reproduces the features of the surface morphology of the cross-section; these features originate from the microtome sectioning of the sample. The intensity of this image is almost a negative of Figure 1A. This image exhibits a ‘brown’ region in the center, suggesting that the presence of CNCs, or other components, significantly reduces the intensity of the Raman band located at ~1296 cm$^{-1}$.

The structural and chemical “fingerprint” of spectroscopic analysis facilitate the conversion of Raman images to chemical images. This yields qualitative information of the regions corresponding to each of the composite components, and the regions where mixing between the components occurs (Figures 2A). The chemical image for the 2.50% CNCs-PEO-HDPE composite confirms the existence of an area with a higher concentration of CNCs within the HDPE matrix; both yellow and blue colours in Figure 1A. The chemical image reveals two distinguishable areas where the CNCs are present. A large yellow area in the center of the aggregate is associated with the master batch of CNCs-PEO. A Raman spectrum corresponding to this region shows the Raman features characteristic of both CNCs and PEO suggesting, that the master batch did not fully disperse in the HDPE matrix during the melt compounding process (Figure 2B - yellow line). A blue area surrounding the yellow center of the aggregate corresponds to the mixing between the CNCs-PEO master batch and the HDPE. The Raman
spectrum observed in this region exhibits bands characteristic of all of the composite components; CNCs, PEO and HDPE (Figure 4B - blue line). The rest of the chemical image is dominated by the polyethylene matrix (Figure 2B - red line).

Figure 2: A typical chemical image of a 2.50% CNCs-PEO-HDPE composite depicting the chemical composition of a mapped cross-section (A). Typical Raman spectra of composite components (B). Spectra shown in B were obtained at positions marked with the crosses at the chemical image (A).

In contrast to high resolution Raman images, the large area Raman images enables a quantification of the spatial distribution of nanofillers in the polyethylene matrix. These images present a larger area of the cross-section of the composite at a lower spatial resolution. Figure 3A shows a typical large area Raman image of a 2.50% CNCs-PEO-HDPE composite. Yellow regions on the image represent areas corresponding to the Raman band located at ~1098 cm\(^{-1}\), typical of CNCs fillers. Their location suggests the random distribution of master batch CNCs-PEO aggregates. The assessment of the population of the aggregates in the image is shown in Figure 3B. Based on two measurements the master batch aggregates exhibit a rather random, or normal distribution. However, more measurements is required to obtain a statistically valid results.
3.2 Multiwalled carbon nanotube fillers

Similar to the analysis of CNCs filled composites, characteristic spectroscopic features are selected for the analysis of MWCNTs-HDPE composites. The best Raman band to differentiate HDPE from the fillers in these composites is a narrow Raman band located at ~1296 cm\(^{-1}\) corresponding to CH\(_2\) twisting modes in the crystalline phase [11, 12]. The first-order G-band located at ~1595 cm\(^{-1}\) is used to confirm the presence of carbon nanotubes [14, 15]. This Raman band is outside of the range of the bands corresponding to HDPE matrix, which facilitate the analysis.

![Figure 4: Typical Raman images of 0.625% MWCNTs-HDPE composite depicting the intensity of Raman band located at ~1595 cm\(^{-1}\) (A) and ~1296 cm\(^{-1}\) (B).](image)

The MWCNTs nanofillers are found to be well-mixed with the HDPE matrix. Figure 4A illustrates the intensity of the Raman band centered at ~1595 cm\(^{-1}\) (the G band) in a cross-section of a 0.625% MWCNTs-HDPE composite. The presence of a brown area on the Raman image verifies the uniform mixing of MWCNTs in the HDPE matrix. The image corresponding to the intensity of the Raman band located at ~1296 cm\(^{-1}\) (CH\(_2\) twisting modes) shows slightly less uniformity (Figure 4B). The image exhibits more yellow areas, where its intensity is higher relative to the filler.

![Figure 5: Typical chemical image of 0.625% MWCNTs-HDPE composite depicting the chemical composition of a mapped cross-section (A). Typical Raman spectra of composite components marked with the white crosses at the chemical image (B).](image)

The chemical image of the 0.625% MWCNTs-HDPE composite clearly displays an effective
mixing between MWCNTs and HDPE. (Figure 5B). The chemical image is dominated by the area corresponding to a mixed phase of MWCNTs and HDPE (green). The spectrum associated with this area exhibits both the D and G Raman bands characteristic for MWCNTs and the bands located at ~1296 cm⁻¹, ~1063 cm⁻¹ and ~1132 cm⁻¹ typical for HDPE (Figure 5B – green line). The Raman spectrum corresponding to the red area on the chemical image confirms a high concentration of HDPE, however is not completely free of bands corresponding to MWCNTs free (Figure 5B - red line spectrum).

4 CONCLUSIONS

The introduction of hydrophilic fillers, such as CNCs, into thermoplastics often results in the formation of nanofiller aggregates, which affects their properties. Raman spectroscopy is a non-destructive and useful tool for chemical and spatial quantification of the mixing process of nanofillers in thermoplastics. The possibility to collect high resolution and large area images delivers unique information about the nanofillers’ distribution, dispersion and the degree of mixing between the nanofillers and the matrix. Raman analysis confirms the presence of the CNCs-PEO master batch aggregates. The interaction with a PEO compatibilizer prevents the formation of pure CNCs aggregates during the melt compounding process. Nevertheless, this compatibilizer is not fully dispersing CNCs in HDPE matrix. In contrast to CNCs-PEO-HDPE composites, MWCNTs containing materials show a high efficiency in the mixing with HDPE.

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