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Raman imaging as a tool for assessing the degree of mixing and the interface between polyethylene and cellulose nanocrystals

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Abstract. The incorporation of spray-dried cellulose nanocrystals (CNCs) into thermoplastics raises the question about the degree of the mixing, given that typically the former are hydrophilic and the latter hydrophobic. Raman imaging has been used as a non-destructive method for the spatial quantification of the mixing process of CNCs in HDPE. A series of polyethylene based composites was prepared by melt compounding using cellulose nanocrystals (CNCs) as a nano-filler. The cross sectional areas of nanocomposite filaments were investigated using confocal Raman microscopy. The degree of mixing between CNCs and HDPE is quantified using this method. It is shown that CNCs have a strong tendency to agglomerate. However, a certain degree of mixing between CNCs and HDPE is observed from Raman images and chemical images obtained by spectroscopy.

1. Introduction

Recent years have brought an increasing interest in nanofillers based on cellulosic forms such as α -cellulose [1,2], cellulose nanofibres (CNF) [3], microcrystalline cellulose (MCC) [4], and cellulose nanocrystals (CNCs) [5] to reinforce thermoplastic polymers including polyethylene (PE). However, the enhancement of mechanical properties requires good mixing of fillers in the matrix and strong interfacial adhesion between both phases. The hydrophilic nature of cellulose induces the formation of hydrogen bonding between the nanoparticles increasing their tendency to agglomerate in polyethylene matrix (hydrophobic). Composites prepared by a melt compounding process typically use maleic anhydride grafted polyethylene (MAPE) as a compatibilizer in order to improve dispersion within and adhesion between the cellulosic fillers and the matrix. The improvement in cellulose dispersion and the increase in the tensile strength of polyethylene composites were reported after the addition of 2-3 wt% of MAPE. The role of MAPE is to interact between cellulose and polyethylene via an esterification reaction and/or hydrogen bonding between the maleic anhydride groups (-COOH and C=O) and the hydroxyl groups (-OH) of cellulose [6]. The ratio of ester linkages to hydrogen bonds depends on the ratio of cyclic anhydride to dicarboxylic acid in MAPE [6]. Additionally, a higher dispersion of cellulose was reported after use of polyoxyethylene (PEO) as a dispersion agent [3,5]. However, the improvement in dispersion did not reflect in an increase of the bending strength and bending modulus of the nanocomposites [3].

The physicochemical and mechanical properties of cellulose-polyethylene nanocomposites have been typically assessed using scanning electron microscopy (SEM) [4,5], differential scanning



calorimetry (DSC) [4,5], thermogravimetric analysis (TGA) [4], dynamic mechanical analysis (DMA) [3], and mechanical tests [3,4]. These evaluations however are not able to quantify the degree of mixing and the interface between thermoplastics and cellulose nanocrystals. Spectroscopic methods such as Raman and IR provide detailed structural and molecular information on composite structure and their morphologies. Development of spectroscopic imaging has increased its potential to describe the composite morphology. Raman imaging has been used to study different types of materials, including cellulose nanocrystals-polypropylene composites [7], biomaterial degradation *in vivo* [8], the characterization of multilayer films [9] and compatibility of polymer blends [10].

In this paper Raman imaging and chemical imaging are used to characterize cellulose nanocrystals-high density polyethylene (CNCs-HDPE) composites containing spray-dried CNCs as fillers. The quantitative evaluation of the mixed and pure composite components gives an answer on the degree of mixing between polyethylene and cellulose nanocrystals. Furthermore, the role and effectiveness of MAPE as a compatibilizer in the melt compounding process is assessed.

2. Experimental

Spray-dried cellulose nanocrystals were purchased from the University of Maine, Process Development Centre; USA. High density polyethylene (Arboblend HDPE) was supplied by Tecnar GmbH, while maleic anhydride grafted polyethylene (A-C 575A, MAPE copolymer) was provided by Honeywell. HDPE composites were prepared by melt-compounding in a counter rotating twin-screw extruder (HAAKE Rheomex CTW5, Thermo Fisher Scientific) which formed filaments with a diameter ~2 mm. Prior to extrusion, the fillers and compatibilizer both in powder form were blended in a mortar for 2 minutes. Subsequently, the powder/HDPE matrix was added and the components were mixed in a mortar for a further 8 minutes. The mixture was dried in a vacuum oven at a temperature of 60 °C for 24h to remove humidity. Composites containing CNCs as fillers were extruded at a temperature of 160 °C. The mixing speed was 70 rpm for 7 min. The CNCs/MAPE/HDPE ratio was 0.625/2.50/96.875, 1.25/2.50/96.25, 2.50/2.50/95.00 and 5.00/2.50/92.50 wt%.

The morphology of the cross-section of the composite filaments was studied using a HITACHI S3200N SEM-EDS scanning electron microscope (SEM) operated at an acceleration voltage of 10 kV. The slices of filament were fixed on metal stubs using carbon tape and sputter-coated at ~20 mA with a ~10 nm layer of gold. The magnifications used for the collection of SEM images were 3000× and 6000×. Raman spectroscopy was performed 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 collect Raman spectra from cross-sections of composite filaments. During the mapping of the CNCs-HDPE composites the power of the laser was ~13 mW. A 50× objective lens was used for backscattered light collection. The spectrometer grating was 600 g/mm, BLZ = 500 nm. Raman images were recorded in an area of 50×50 μm² with a step size of 0.2 μm and an exposure time of 0.1 s and one accumulation. A total of 62500 Raman spectra were measured for each map. The average number of maps per composite was six. WITec Project Plus software was used to analyze Raman images and to convert them into chemical images. These chemical images were subsequently analyzed using Image-J software to estimate the area in μm² and the percentage of the area related to each component of the chemical image. The extraction of the objects was performed using an automated threshold with the algorithm IsoData.

3. Results and Discussion

The morphologies of the cross-sectional areas of HDPE composites were investigated using scanning electron microscopy (SEM). Figure 1 illustrates the representative SEM images of HDPE composites containing 1.25% of CNCs (Figure 1A and C) and 5.00% of CNCs (Figure 1B and D) at different magnifications. The surfaces of the cross-sectional areas is smooth with evident cellulose nanocrystals aggregates present within the volume of the matrix. Spray-dried CNCs fillers form spherical-like aggregates in polyethylene, Figure 1. Additionally, SEM images reveal the presence of empty spaces

near the spherical CNCs aggregates. These voids probably derive from poor interfacial adhesion between CNCs and HDPE [1]. Another reason for their formation is the process of the cryo-microtome cutting at a temperature of -22°C , since the orientation of the main axis of the voids is consistent with the direction of cutting. The process of cutting above the glass transition temperature of HDPE can potentially induce a ‘drawing out’ of the aggregates from the matrix. The existence of some interaction between CNCs and HDPE seems to be supported by the higher magnification images (Figure 1C and D). These images show broken filaments between CNCs aggregates and HDPE matrices. SEM images confirm the formation of aggregates of CNCs in HDPE and the existence of some interaction between nano-fillers and the matrix.

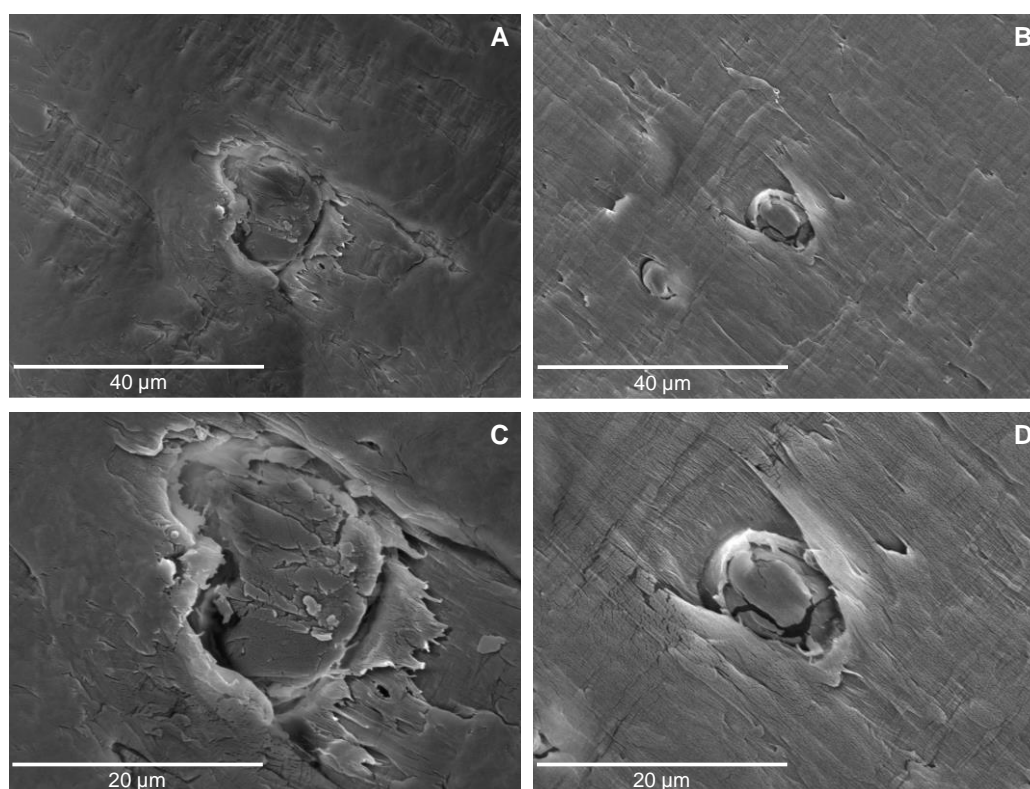


Figure 1. SEM images of cryo-microtome cut CNCs-HDPE composites at a magnification $3000\times$ (A) 1.25% CNCs-HDPE, (B) 5.00% CNCs-HDPE and at a magnification $6000\times$ (C) 1.25% CNCs-HDPE, (D) 5.00% CNCs-HDPE.

The cross-sectional areas of CNCs-HDPE composites were investigated using Raman imaging. The advantage of Raman spectroscopy is its sensitivity to structural and chemical features of the studied materials. The combination of the spectroscopic analysis with optical microscopy facilitates an estimation of the degree of mixing and the interface between the fillers and the matrix.

The HDPE matrix is differentiated from the CNCs by a narrow Raman band located at $\sim 1296\text{ cm}^{-1}$ corresponding to CH_2 twisting modes in the crystalline phase [11,12]. The presence of CNCs is verified by the Raman band located at $\sim 1098\text{ cm}^{-1}$, 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 [13,14]. This feature is absent in HDPE.

Figures 2 and 3 show Raman images of CNCs-HDPE composites. The color scale present on each of the Raman images depicts the relative intensity of selected Raman bands. A yellow color indicates a high intensity of a specific band, whereas a dark color a low intensity. Figure 2 shows Raman images of CNCs-HDPE composites highlighting the intensity of a Raman band located at $\sim 1098\text{ cm}^{-1}$. The

yellow colored fields forming spherical-like shapes correspond to aggregates of CNCs. The shape of the aggregates is similar for all the images and is independent of the loading of CNCs in the composites. This suggests that the fillers' aggregation is related to the spray-drying process used for their preparation. It is noted that the changes in the intensity of the Raman band located at $\sim 1098\text{ cm}^{-1}$ reflect the features of the surface morphology of the aggregates. Raman images presented in Figure 3 show almost the negatives of images in Figure 2. They show the presence of the HDPE matrix using the relative intensity of a Raman band situated at $\sim 1296\text{ cm}^{-1}$. These images also reveal the surface morphology including features originating possibly from the blade of the knife used for cryo-microtome cutting.

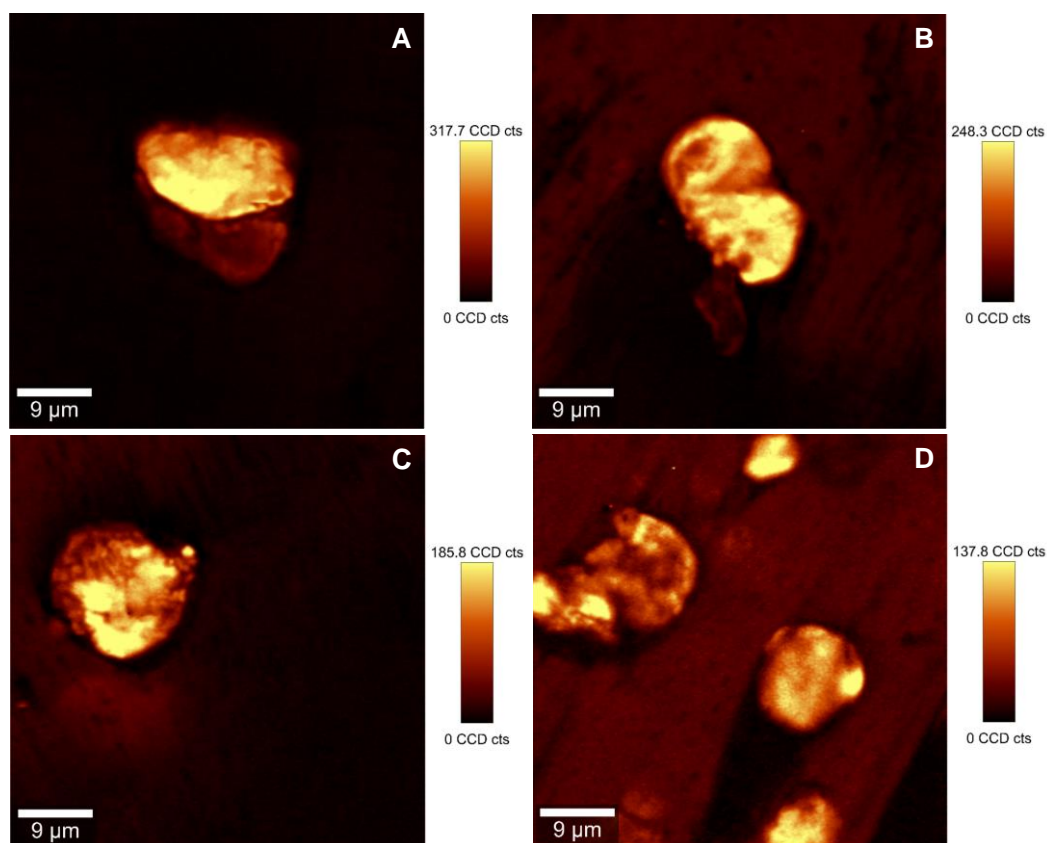


Figure 2. Typical Raman images of CNCs-HDPE composites depicting the intensity of a Raman band located at $\sim 1098\text{ cm}^{-1}$: (A) 0.625% CNCs-HDPE, (B) 1.25% CNCs-HDPE, (C) 2.50% CNCs-HDPE, (D) 5.00% CNCs-HDPE.

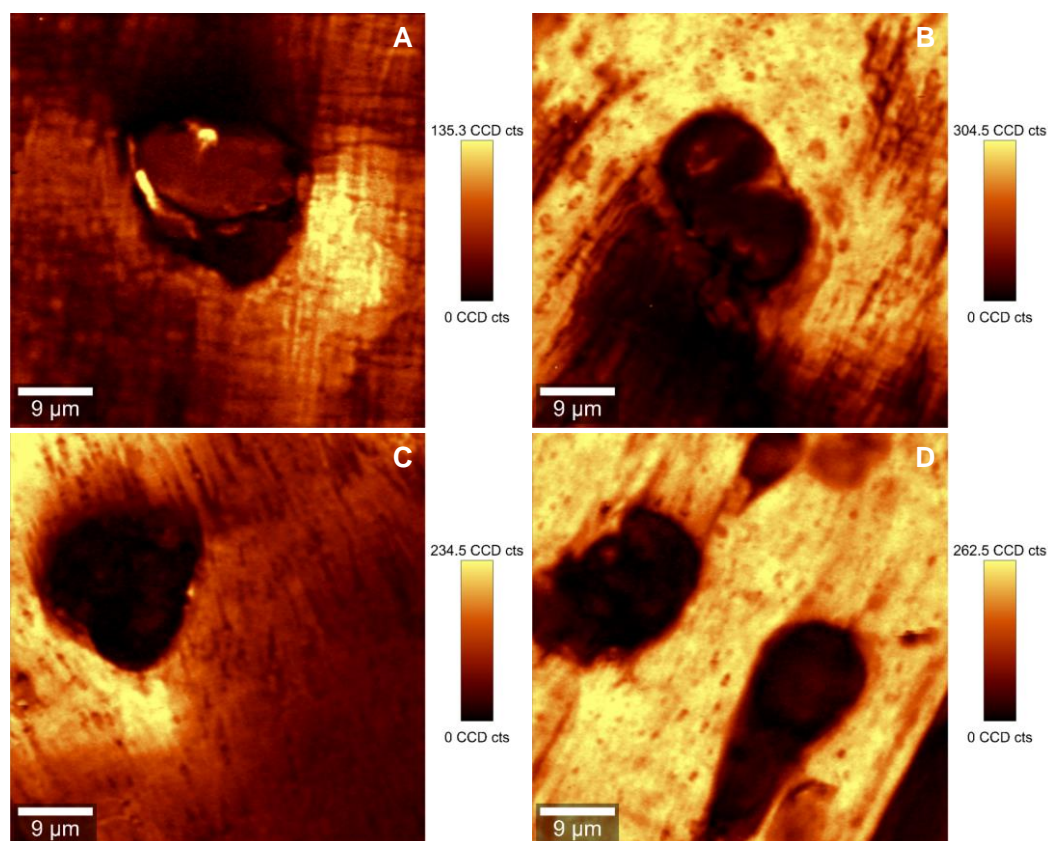


Figure 3. Typical Raman images of CNCs-HDPE composites depicting the intensity of a Raman band located at $\sim 1296\text{ cm}^{-1}$: (A) 0.625% CNCs-HDPE, (B) 1.25% CNCs-HDPE, (C) 2.50% CNCs-HDPE, (D) 5.00% CNCs-HDPE.

Figure 4 shows typical Raman spectra for the components of the compounded composites. A map of these components transforms them into chemical images showing the regions corresponding to the composition of the composites. It also demonstrates where mixing between the components occurs (Figure 5). The chemical images reveal three major areas present in the CNCs-HDPE composites. Two of them correspond to the pure CNCs (green area) and pure HDPE (red area), which is confirmed by the Raman spectra on Figure 4. Green line Raman spectrum on Figure 4 shows bands characteristic of pure CNCs proving the formation of agglomerates of CNCs in the volume of polyethylene matrix independently of the loading of CNCs in the composites. The areas corresponding to pure HDPE matrix dominate the chemical maps of the composites with different loading (Figure 4 - red line). The most significant for the composite preparation is the blue area on the chemical maps associated with the mixing between CNCs and HDPE. A Raman spectrum corresponding to this region exhibits the bands characteristic of both CNCs and HDPE suggesting a good mixing of the components (Figure 4 - blue line). Despite the presence of the area where mixing between CNCs and HDPE occurring, the chemical images verify once again the tendency of cellulose to aggregate within the HDPE matrix. The aggregates of CNCs consist of both pure CNCs (green area) and mixed CNCs and HDPE (blue area).

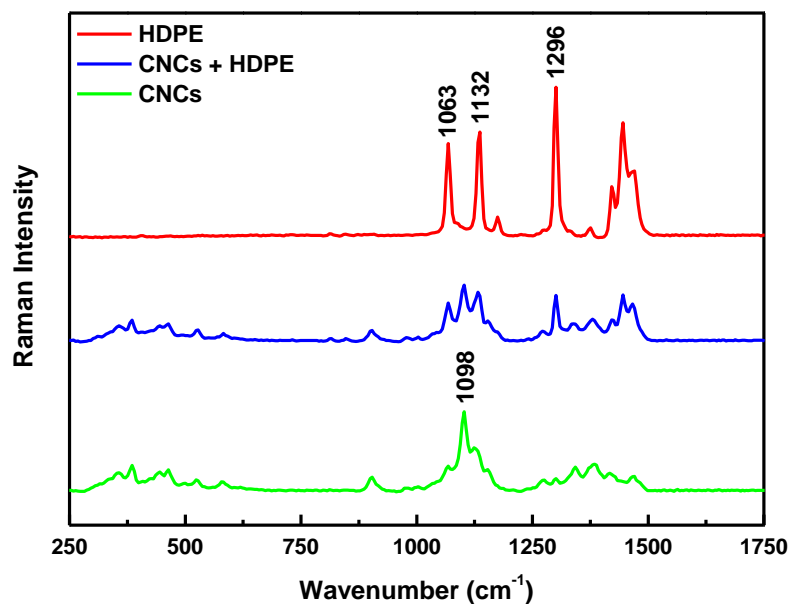


Figure 4 Typical Raman spectra of composite components. The colors used here map onto to the chemical image of 5.0% CNCs(FR)-HDPE in Figure 5C.

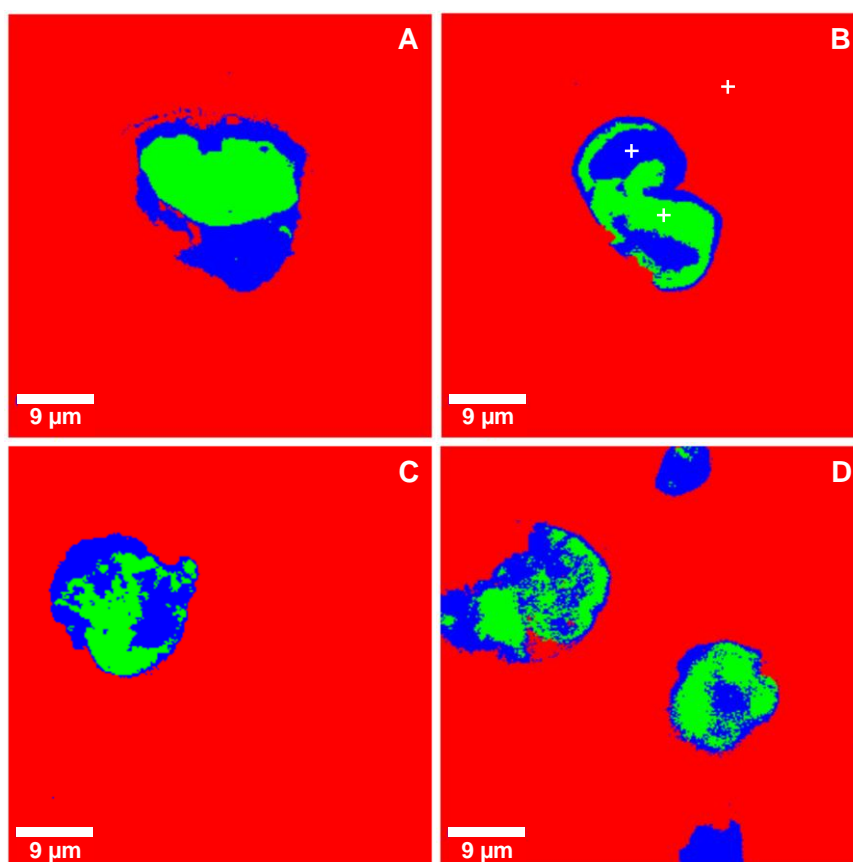


Figure 5. Typical chemical image of 1.25% CNCs-HDPE composite depicting the chemical composition of a mapped cross-section: (A) 0.625% CNCs-HDPE, (B) 1.25% CNCs-HDPE, (C) 2.50% CNCs-HDPE, (D) 5.00% CNCs-HDPE.

The chemical images are used for a statistical assessment of the area corresponding to each of the composite components. Image-J software is used to quantify the area (in μm^2) related to the components (Table 1). The ratio of the fraction of the mixed areas (fillers and matrix) to the areas of pure matrix quantifies the effectiveness of the degree of mixing. The average ratio of the Blue:Red area for CNCs-HDPE composites with different loadings of CNCs is comparable. Since the loading of MAPE compatibilizer is the same for the entire series of composites, it poses an additional limiting factor for increasing the efficiency of mixing between CNCs and HDPE. This suggests that the process of the preparation of CNCs plays an important role in their incorporation into the matrix. The hydrophilic nature of CNCs induces the formation of hydrogen bonding between the nanoparticles increasing their tendency to agglomerate in nonpolar matrices. Additionally, a compact form of the CNCs reduces their ability to mix with the HDPE matrix through their interaction with macromolecules of MAPE and HDPE.

Table 1. Average area fraction of the component of chemical maps quantified using Image J software.

Composite	Area fraction			Ratio of fraction	
	Red ^a [μm^2]	Blue ^b [μm^2]	Green ^c [μm^2]	(Green+Blue)/Red	Blue/Red
0.625% CNCs-HDPE	2282 ± 84	74 ± 26	112 ± 77	0.08 ± 0.04	0.06 ± 0.05
1.25% CNCs-HDPE	2238 ± 102	121 ± 88	107 ± 27	0.10 ± 0.05	0.06 ± 0.04
2.50% CNCs-HDPE	2265 ± 85	105 ± 40	97 ± 81	0.09 ± 0.04	0.05 ± 0.02
5.00% CNCs-HDPE	2220 ± 101	148 ± 54	100 ± 66	0.11 ± 0.05	0.07 ± 0.03

^a fraction area corresponding to HDPE.

^b fraction area corresponding to CNCs + HDPE.

^c fraction area corresponding to CNCs.

4. Conclusions

In recent times there has been a lot of interest in making composites using renewable and biodegradable components. Both bio-polyethylene and cellulose fulfill these criteria. However, high quality composites require good mixing between the filler and the matrix to obtain good interfacial adhesion, and consequently optimize the reinforcing effect of the fillers. Raman microscopy is a non-destructive and useful tool for chemical and spatial quantification of the mixing process of CNCs in HDPE. The data provided by the analysis of Raman images and chemical images includes spatial information regarding the agglomeration of CNCs and the surface morphology features of composites. CNCs are found to form agglomerated 'islands' within the HDPE independent of the filler loading. Raman microscopy has been demonstrated to be able to quantify the degree of mixing between CNCs and HDPE. The quantified degree of mixing for a series of composites shows a comparable degree of mixing for all of the materials. It suggests that for the incorporation process of CNCs into thermoplastics with addition of compatibilizer is equally important as the physicochemical properties and morphology of the filler.

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