

Linear Low-Density Polyethylene Colored with a Nanoclay-Based Pigment: Morphology and Mechanical, Thermal, and Colorimetric Properties

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ABSTRACT: In this study, a novel kind of hybrid pigment based on nanoclays and dyes was synthesized and characterized. These nanoclay-based pigments (NCPs) were prepared at the laboratory with sodium montmorillonite nanoclay (NC) and methylene blue (MB). The cation-exchange capacity of NC exchanged with MB was varied to obtain a wide color gamut. The synthesized nanopigments were thoroughly characterized. The NCPs were melt-mixed with linear low-density polyethylene (PE) with an internal mixer. Furthermore, samples with conventional colorants were prepared in the same way. Then, the properties (mechanical, thermal, and colorimetric) of the mixtures were assessed. The PE–NCP samples developed better color properties than those containing conventional colorants and used as references, and their other properties were maintained or improved, even at lower contents of dye compared to that with the conventional colorants. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2716–2726, 2013

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INTRODUCTION

During the last few decades, organically modified clays have been widely studied as reinforcing additives to improve the mechanical, barrier, and thermal properties in different substrates.^{1–3} Related to these kind of nanoadditives, Fischer and Batenburg^{4–6} (from TNO-TPD) developed a new type of hybrid pigment obtained from a combination of organic dye molecules and layered clay nanoparticles, especially phyllosilicates from the smectite group. They claimed that these nanoadditives benefitted from the advantages of dyes, such as bright colors and a wide color gamut and avoided their drawbacks, such as low lightfastness and low stability against oxygen, temperature, and UV radiation. Moreover, these new materials were free of heavy metals that some conventional colorants possess.^{7,8}

Nanoclay-based pigments (NCPs) could be used with a wide variety of substrates to make coatings or to color materials, but some applications have not been developed yet. At present, great interest in nanoclays for polymers has especially been focused on the enhancement of the physical and chemical properties of nanocomposites. However, new NCPs are expected to improve those properties while giving color and making it possible to reduce the amount of additives used and, thereby, the cost.

Polyethylene (PE) is one of the most demanded thermoplastics, and it has been applied to a large variety of fields (packaging, construction, electronics, etc.). Furthermore, PE/clay nanocomposites have been widely studied.^{9–16} However, PE is a nonpolar polymer, and thus, the compatibility between nanoclays and PE is very low, so it is difficult to achieve a good level of exfoliation of the nanoclay (NC) sheets in the polymeric matrix. Apart from the modification of the clay with organic molecules, it is necessary to add a compatibilizer to increase the interactions between PE and NC. In this way, an appropriate level of dispersion or exfoliation and then an optimal development of the nanocomposite properties can be achieved. Although maleic anhydride grafted polyolefins are the most widely used type of compatibilizer used for nonpolar polymers such as PE and polypropylene,^{10–16} in some studies, oxidized PE^{17,18} or polymers grafted with organosilanes^{19,20} have been used.

In a previous study,²¹ we demonstrated the suitability of NCP as a new type of colorant for PE. In that study, the mechanical properties and color performance of linear low-density polyethylene (LLDPE) mixed with an as-synthesized NCP were compared with the behavior of LLDPE mixed with other conventional pigments. Both the NCP and the conventional pigments were used at very low concentrations (0.1 phr).

To our knowledge, in all the published works about polymer–clay nanocomposites, the modification of the NC has been done by the replacement of the total cation-exchange capacity (CEC) by an organic surfactant. In this study, a series of NCPs was synthesized with various fractions of the CEC of the NC interchanged with dye, from 1 to 100%. The idea was to increase the interlayer distance in the NC by the inclusion of the dye and the compatibility between the polymeric matrix and NC but also to obtain a wide color gamut. Thus, several NCPs were prepared at the laboratory, and their full characterization was carried out. The obtained NCP and two conventional colorants were melt-blended with LLDPE at concentrations varying from 0.1 to 5 phr. An organosilane-based compatibilizer was used in some formulations. The morphology, mechanical strength, thermal stability, and optical properties of the samples obtained were assessed.

EXPERIMENTAL

Materials

LLDPE Elite 5610 (PE; density = 0.917 g/cm³ and melt flow index = 4.5 g/10 min) was supplied by Dow Chemical (USA). The compatibilizer (C) used in some samples contained an organosilane, vinyl trimethoxysilane, supplied by Quimidroga S. A. (Spain), and a dicumyl peroxide, bis(α,α -dimethyl benzyl) peroxide, supplied by Sigma-Aldrich (USA). The NC used (N) was Nanofill 116 provided by Süd-Chemie (Germany). Nanofill 116 was a sodium montmorillonite with a CEC of 120 mequiv/100 g of clay. The organic colorant used as a surfactant was methylene blue (MB; C₁₆H₁₈ClN₃S 3H₂O; molecular weight = 319.85 g/mol) supplied by Sigma-Aldrich (Germany). Blue Ultramarine (BU supplied by Nubiola Pigments S. L., Spain) was used as a conventional inorganic pigment for PE.

Preparation of the NCPs

The synthesis of the blue nanopigments on the laboratory scale was carried out according to the method proposed by Fischer and Batenburg.⁶ An amount of 10 g of NC was dispersed in 2 L of deionized water under vigorous stirring for 24 h. In this way, the distance between the clay sheets increased, and as a consequence, the ionic bond forces of the interlayer counter ions were reduced. After that, a solution of colorant was added to the dispersion with stirring maintained for 1 h. The ionic exchange took place, and the molecules of the dye replaced the sodium counter ions. The next steps were washing, filtering, and drying (through freeze drying for 8 h at 2×10^{-3} mbar and -70°C), and a blue material collected. As a result, a light powder was obtained.

In this study, four different types of NCP were prepared. The quantity of MB dissolved in the solution of colorant added to the dispersed NC depended on the percentage of the CEC that was intended to be exchanged. The percentages of the CEC of the NC exchanged with MB were 1, 5, 20, and 100% (milliequivalents of MB per gram of NC), and the obtained materials were named s NCP(1), NCP(5), NCP(20), and NCP(100), respectively. According to the NC CEC, these NCPs nominally contained 0.3, 1.7, 6.8, and 34.1 g of MB/100 g of NC, respectively.

Preparation of the PE Samples

The PE samples were prepared by melt blending. Polymer and additives in powder state were first mechanically premixed in a Thermomix Vorwerk 3300 (Germany) instrument for 2 min at

medium speed. Then, the mixture was blended in a Brabender Plasticorder PL 2000 internal mixer (Germany) for 10 min at 170°C and with a 40-rpm counterrotational blade speed.

To improve the dispersion of the clay, a compatibilizer was added to half of the prepared samples. The compatibilizer mixture contained 100 phr of LLDPE, 1 phr of vinyl trimethoxysilane, and 0.1 phr of dicumyl peroxide, and it was melt-blended in the Brabender Plasticorder under the conditions described previously. When added, the compatibilizer was always in a proportion of NC to compatibilizer of 1 : 3.

Finally, thin sheets approximately 1 mm thick were prepared in a Mecamaq PHF 50 hot plate press under these conditions: 20 min of heating without pressure and with the mold opened, 5 min of heating with the mold closed, and then 30 s with a pressure of 80 bar. Samples were cooled in a plate press refrigerated with water at 10°C for 12 min.

All of the samples prepared and their compositions are shown in Table I. The nomenclature of the samples was as follows: PE designates the polymer; NC is the unmodified NC; NCP(*X*) indicates the nanopigment, where *X* is the percentage of CEC exchanged with MB; and separated by a hyphen is the concentration of additive in parts per hundred of polymer in the sample. The samples that contain compatibilizer include a C at the end of the name.

Sample Characterization

Elemental Analysis. Elemental analysis was carried out to determine the actual quantity of MB exchanged in the NC. A CHNS elemental analyzer fitted with a Micro TruSpec detector from LECO (USA) was used. The sulfur content of the synthesized NCP was used to calculate the actual amount of MB interchanged.

X-ray Diffraction. X-ray diffraction data were obtained by a Bruker D8-Advance diffractometer (Germany) equipped with a Göebel mirror, a high-temperature chamber, and a Kristalloflex K 760-80F X-ray generator. Samples were scanned in the 2θ range from 2 to 10° at a scanning rate of $1^\circ/\text{min}$ with Cu K α X-ray radiation ($\lambda = 1.540$ nm, 40 kV, 40 mA) at room temperature. The basal spacing of the NC layers (*d*) was calculated with the Bragg equation:

$$\lambda = 2d \sin \theta$$

Microscopy. Micrographs were taken with a transmission electron microscope (JEOL JEM-2010, Japan) operating at 200 kV and equipped with a OIRUS SC600 camera (GATAN, UK). The ultrathin sections for transmission electron microscopy (TEM) were cut by an RMC model MTXL ultramicrotome. Furthermore, scanning electron micrographs were taken with a JEOL JSM-840 scanning electron microscope (Japan).

Mechanical Strength. Tensile tests were performed with an Instron model 4411 tensile tester (Italy) with digital data acquisition. Tests were carried out at room temperature and at a speed of 25 mm/min. Young's modulus (*E*), elongation, strain, and load at the breaking point were determined as average values of five to eight tensile specimens, which were obtained with a die cutter from the thin sheets. The cross section of each specimen was about 5×1 mm², and the whole length was 70 mm.

Table I. List of PE Samples Prepared with Nanoclay, NCP, and Conventional Colorants

Set of samples	Sample	NC/NCP	MB	BU	Compatibilizer
PE-C	PE	—	—	—	—
	PE-C-0.3	—	—	—	0.3
	PE-C-3	—	—	—	3
	PE-C-15	—	—	—	15
PE-MB	PE-MB-0.1	—	0.1	—	—
	PE-MB-1	—	1	—	—
PE-BU	PE-BU-0.1	—	—	0.1	—
	PE-BU-1	—	—	1	—
	PE-BU-5	—	—	5	—
PE-NC	PE-NC-0.1	0.1	—	—	—
	PE-NC-1	1	—	—	—
	PE-NC-5	5	—	—	—
	PE-NC-0.1-C	0.1	—	—	0.3
	PE-NC-1-C	1	—	—	3
	PE-NC-5-C	5	—	—	15
PE-NCP(1)	PE-NCP(1)-0.1	0.1	—	—	—
	PE-NCP(1)-1	1	—	—	—
	PE-NCP(1)-5	5	—	—	—
	PE-NCP(1)-0.1-C	0.1	—	—	0.3
	PE-NCP(1)-1-C	1	—	—	3
	PE-NCP(1)-5-C	5	—	—	15
PE-NCP(5)	PE-NCP(5)-0.1	0.1	—	—	—
	PE-NCP(5)-1	1	—	—	—
	PE-NCP(5)-5	5	—	—	—
	PE-NCP(5)-0.1-C	0.1	—	—	0.3
	PE-NCP(5)-1-C	1	—	—	3
	PE-NCP(5)-5-C	5	—	—	15
PE-NCP(20)	PE-NCP(20)-0.1	0.1	—	—	—
	PE-NCP(20)-1	1	—	—	—
	PE-NCP(20)-5	5	—	—	—
	PE-NCP(20)-0.1-C	0.1	—	—	0.3
	PE-NCP(20)-1-C	1	—	—	3
	PE-NCP(20)-5-C	5	—	—	15
PE-NCP(100)	PE-NCP(100)-0.1	0.1	—	—	—
	PE-NCP(100)-1	1	—	—	—
	PE-NCP(100)-0.1-C	0.1	—	—	0.3
	PE-NCP(100)-1-C	1	—	—	3

Thermogravimetric Analysis. A PerkinElmer Pyris TGA 7 Thermogravimetric Analyzer (USA) was used. The conditions were as follows: preheating for 10 min at a constant temperature of 30°C and heating from 30 to 600°C at a rate of 10°C/min in a nitrogen atmosphere at a 10 mL/min flow rate. The initial weight of the samples was between 5 and 7 mg.

Bleeding Test. A bleeding test was carried out according to the standard ASTM D 279-2 standard test method for the bleeding of pigments. A plaque of the colored polymer was pressed against sheets of plasticized poly(vinyl chloride) (PVC) with 0.1 wt % TiO₂ in a sandwich configuration. The sandwich was placed into

an oven at 100°C for 1 h. If the PVC sheets were stained by the dye, the result of the test was positive (i.e., there was migration).

Color Performance. The hiding power (D) and coloring power (Φ) of the colored samples were calculated by application of the theory of Kubelka–Munk for two fluxes. Therefore, the reflectance spectra over the white and black substrate (which was a white and black cardboard sheet) were measured with a spectrophotometer CM-2600d Konica Minolta (Spain). The reflectance spectra of the black and white substrates were also measured. Measurements were taken with a D65 light source [2° observer,

Table II. Nominal and Actual MB Contents of the Synthesized Nanopigments

Nanopigment	Nominal CEC with MB (%)	Nominal weight of MB per 100 g of N	Actual weight of MB per 100 g of N (by CHNS)
NCP(1)	1	0.3	0.23
NCP(5)	5	1.7	0.87
NCP(20)	20	6.4	5.2
NCP(100)	100	25.4	24.8

UV excluded (0%), and specular component included].²² These color performance parameters could be defined as follows:

- D (m^2/L), is the ability to hide the color or color difference (ΔE^*_{ab}) of the substrate. It can be determined by the inverse of the thickness of the film (h_D), which causes a ΔE^*_{ab} equal to 1 in the substrate:

$$D = \frac{1}{h_D} \Big|_{\Delta E^*_{ab}=1} \quad (1)$$

- Φ (m^2/L) is the ability to give color. Φ is determined by the ΔE^*_{ab} that takes place when there is an infinitesimal variation in the thickness (h) of a film applied on a white substrate:

$$\Phi = \frac{d\Delta E^*_{ab}}{dh} \Big|_{\substack{\text{white substrate} \\ h=0}} \quad (2)$$

Colorfastness. An accelerated weather test was applied to assess the ability of the NCP to maintain the color when the samples were exposed to weather conditions (light, water, and heat). It was done in a Solarbox 1500e HR laboratory test chamber (Neurtek, Spain). The test was carried out according to the ASTM D 2565-99 (“Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications”) under the followings conditions for each cycle: 102 min of light only ($0.35 \pm 0.02 \text{ W/m}^2$ at 340 nm and $41.5 \pm 2.5 \text{ W/m}^2$ from 300 to 400 nm) at $63 \pm 2^\circ\text{C}$, followed by 18 min of light with water spray. This cycle was repeated for 504 h. Every 24 h (or 12 cycles), the reflectance spectra of the samples were measured, and then, the CIE- $L^*a^*b^*$ color system coordinates and the color differences (ΔE^*_{ab} , ΔL^* , Δa^* , and Δb^*) for each original sample were calculated. ΔL^* , Δa^* , and Δb^* represent the differences in lightening, the green–red component, and the blue–yellow component, respectively. A positive value of ΔL^* indicates a lightening in the sample, whereas a negative value indicates a darkening in the sample. A positive Δa^* signifies a color shift toward red, and a negative value indicates a color shift toward green. In the same way, a positive Δb^* means a shift toward yellow, and a negative Δb^* means a shift toward blue. ΔE^*_{ab} represents the global color change, which is calculated according to the following equation:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^* + \Delta a^* + \Delta b^*)^2} \quad (3)$$

RESULTS AND DISCUSSION

Morphology

The actual amount of MB exchanged in the NC for the different synthesized NCPs was calculated from the sulfur content

obtained by CHNS analysis. The results are shown in Table II. In all cases, the amount of cation adsorbed was lower than the nominal amount. The MB exchanged for the NCP(100) was consistent with the amounts obtained by Jankovic et al.,²³ who synthesized organomontmorillonites using cations with different structures, some containing benzene rings, such as MB. According to Table II, the actual amounts of MB in the synthesized nanopigments were 0.2, 0.9, 5.2, and 24.8 wt %.

In addition, X-ray diffraction tests were performed to assess the modification in the interlamellar distance of the NC as a consequence of the cationic exchange with MB. Figure 1 shows the XRD patterns of the NC and the nanopigments [NCP(X)] prepared at the laboratory. Even for NCP(1), there was an important displacement in the XRD peak of NC. In general, the greater the percentage of CEC exchange was, the more the peak shifted to lower angles. That indicated that the basal spacing (d_{001}) and therefore the interlamellar distance in the clay sheets increased as the content of MB increased. Nevertheless, the displacement of peaks was not uniform with the percentage of MB interchange, and a major displacement was found for the NPC(20) nanopigment. Xi et al.²⁴ modified sodium montmorillonite with different amounts of an alkyl ammonium surfactant. They also found that the basal spacing increased as the amount of the CEC interchanged increased, and like in our results, there were some exceptions at different levels of CEC exchange (20–40% of the CEC). They proposed that for relatively low amounts of sodium interchanged by the surfactant, the high hydration of sodium could make the basal spacing higher than when there was more sodium replaced by the surfactant; this helped to explain the greater interlamellar distance that we found for NCP(20) than NCP(100).

In the scanning electron micrographs shown in Figure 2, it is possible to identify some changes that the NC suffered because of the exchange process. NC had a structure of compacted clay sheets, whereas in NCP(100), the clay sheets were smaller and more separated.

XRD tests were carried out to determine the degree of exfoliation or intercalation of the NC in the composites prepared with PE. For example, Figure 3 shows the diffraction diagram for the set of PE samples with different concentrations of NCP(1) [PE–NCP(1)]. In all of the samples, the effect of the concentration

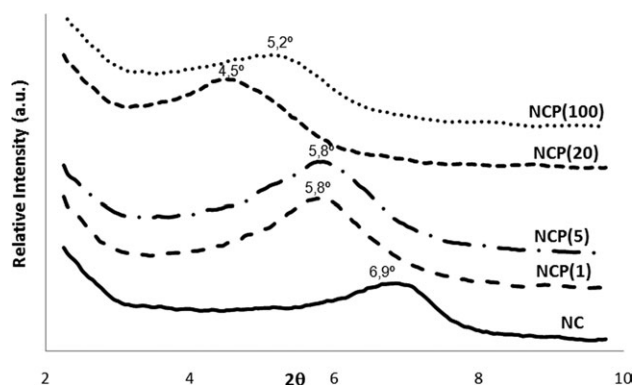


Figure 1. XRD patterns of the NC and nanopigments [NCP(X)].

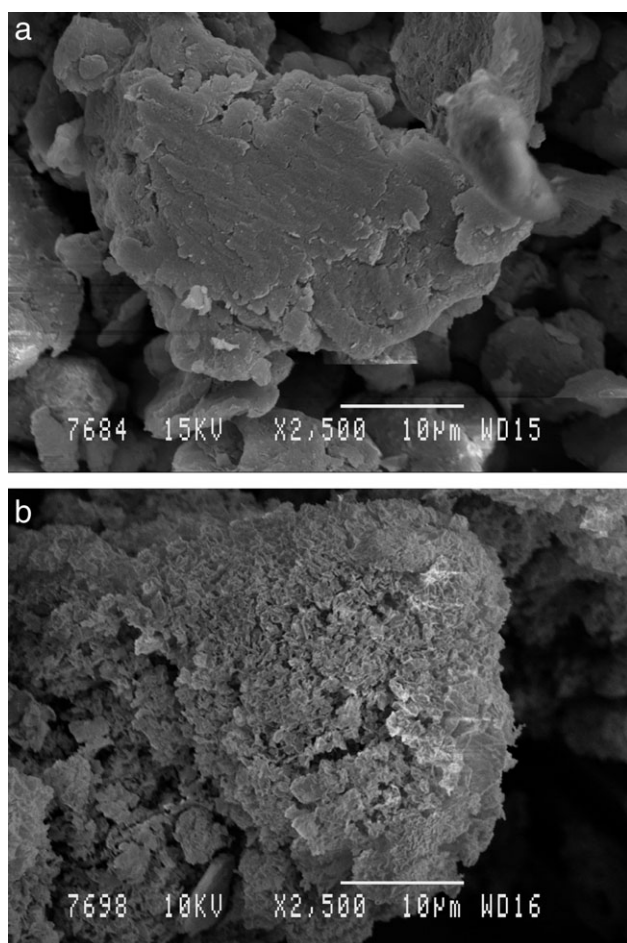


Figure 2. Scanning electron micrographs of (a) unmodified NC and (b) nanopigment with 100% of CEC exchanged [NCP(100)].

of nanoadditives was similar; as the concentration of NC or nanopigment increased, the height of the diffraction peak increased. When the samples with and without compatibilizer were compared, the samples with compatibilizer had a slightly higher peak height.

Table III shows the positions of the diffraction peak and the corresponding interlayer distances of the NCP(*X*) and that of the samples with PE and 5 phr of the additives. For the samples with a low level of CEC interchanged, PE–NCP(1) and PE–NCP(5), the peak position in the mixture with the polymer was the same as in the pristine nanopigment, independently of the NCP(*X*) concentration. Shah and Paul¹⁰ also described no displacement of the diffraction peaks in the polymer nanocomposites with respect to the organoclay. This indicated that although the polymer chains could have penetrated the clay sheets, the interactions of the polymer with the clay lamellae may have been weak, and the samples may have had an intercalated structure. Figure 4 shows the TEM photographs of some of the samples with PE and NCP(*X*), which confirmed the intercalated structures. Nevertheless, the position of the XRD peak in the PE–NCP(20) series shifted toward higher angles in comparison to the peak of NCP(20) (see Table III), and this implied a lower clay sheet distance. The same could be observed for the PE–NCP(100) series,

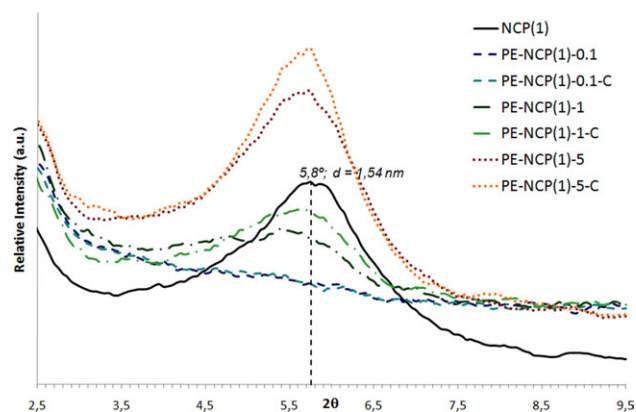


Figure 3. XRD patterns of the set PE–NCP(1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but it was less marked. This phenomenon has been described by other authors for PE plus modified nanoclays systems.^{11,16,17,25} To explain it, it has been suggested that the degradation and loss of the organic surfactant in the modified NC could take place during processing and would produce the collapse of the clay sheets and, consequently, a shift of the XRD peak toward higher 2θ . In our case, the thermal stability of methylene was much higher than that of the quaternary ammonium salts that are commonly used as surfactants. Consequently, samples of these series showed good thermal stability, as shown later. If MB molecules left the interlamellar spaces between the NC in the PE–NCP(20) and PE–NCP(100) composites, as a consequence of the thermal treatment and the applied shear, they may have remained on the NC surface or in the polymer matrix. On the other hand, the higher displacement of the XRD peaks in the composites obtained with NCP(20) compared to that with NCP(100) was in accordance with the higher hydration of NCP(20), as discussed previously. The release of water may explain the higher displacement of the XRD peak of PE–NCP(20).

Mechanical Strength

Table IV shows the values of E (MPa) and Table V shows the values of the energy at break (E_{abs} ; J) of the composites

Table III. XRD Peak Positions and Interlayer Distances in the NCP and the Set of Samples of PE and 5 phr NCP

	Diffraction peak (2θ)	d_{001} (nm)
NC	6.85	1.30
PE–NC	6.85	1.30
NCP(1)	5.75	1.54
PE–NCP(1)–5	5.75	1.54
NCP(5)	5.8	1.51
PE–NCP(5)–5	5.85	1.51
NCP(20)	4.5	1.96
PE–NCP(20)–5	6	1.47
NCP(100)	5.1	1.73
PE–NCP(100)–5	5.4	1.64

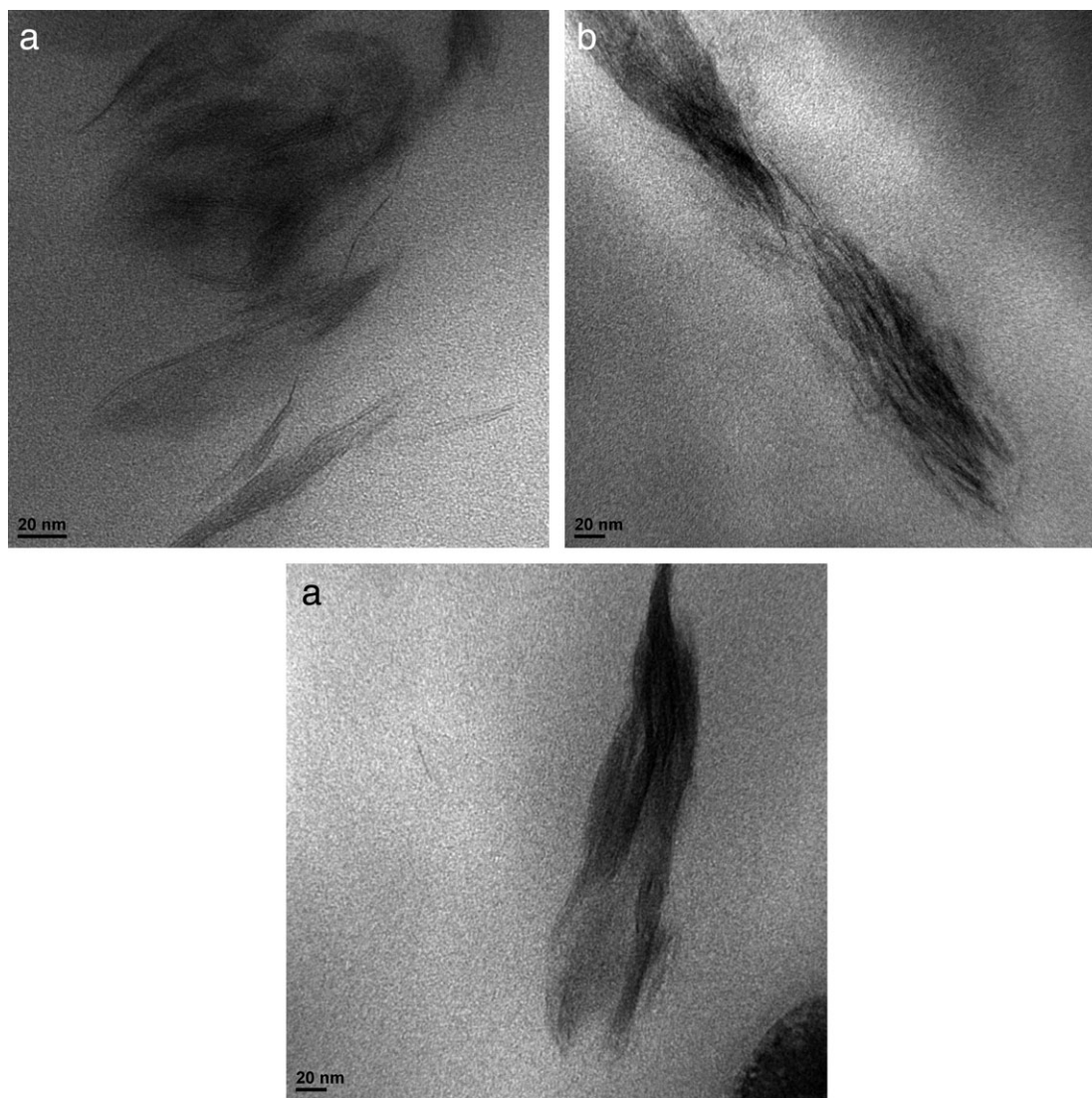


Figure 4. TEM images of the (a) PE-NCP(5)-5-C, (b) PE-NP(20)-0.1-C, and (c) PE-NCP(100)-1-C samples.

prepared. In general, two tendencies could be identified. Samples prepared with only 0.1 phr NC or NCP(1) and NCP(5) (a low load of MB) presented values of E and E_{abs} that were higher than the ones of PE. However, when the concentration of the nanoadditive increased, there was a decrease in the values of E and E_{abs} . On the other hand, samples prepared with NP(20) and NP(100) (a high load of MB) had lower values of E and E_{abs} than PE, and they showed an uncertain trend as the concentration of the nanopigment in the samples increased. It is generally accepted that there will be an increase in E with the load of organoclay and compatibilizer,^{1,26} whereas the ductility (related to E_{abs}) in general decreases when the concentration of organoclay increases.^{21,27,28} However, increases in E and the ductility have also been described for LDPE/LLDPE/NC systems.¹⁶ In any case, the mechanical properties of nanocomposites depend on its morphology and on the interaction between the components (polymer, compatibilizer, and organoclay).

When the compatibilizer was incorporated into the sample, the values of E and E_{abs} increased (Tables IV and V). In some cases,

there was an increase of 60% compared to the sample without compatibilizer. Therefore, the presence of the compatibilizer improved the mechanical response of the LLDPE samples.

For the conventional colorants used as references (MB and BU), the moduli increased as the concentration of the colorant increased (Table IV). The higher increase of the moduli was for the sample PE-BU-5 ($\leq 30\%$ of the value of PE), which presented a moduli similar to the samples containing 1 or 5 phr PE-NCP(X)-C. For the pigment BU, the E_{abs} value (Table V) was similar to those of the samples with NCP and much higher than those of the samples containing MB as a colorant.

Thermal Stability

In general, there were no significant differences in the thermal stability of the PE-NCP(X) samples compared to that of PE. All of the sets showed similar behavior: at about 380°C, the degradation process started, and the maximum degradation rate was about 480°C. Those samples with the highest NC or NCP content showed a small loss of mass ($<0.5\%$) around 60–150°C

Table IV. *E* Values for PE Mixtures with and Without Compatibilizer and with Nanoclay and Those Colored with NCP(X), MB, and BU

Sample	<i>E</i> (MPa)	Sample	<i>E</i> (MPa)
PE	135.7 ± 5.4	PE-C-0.3	162.9 ± 2.7
		PE-C-3	184.2 ± 3.9
		PE-C-15	148.3 ± 2.2
PE-NC-0.1	163.9 ± 4.9	PE-NC-0.1-C	170.6 ± 5.2
PE-NC-1	159.6 ± 1.6	PE-NC-1-C	161.9 ± 2.4
PE-NC-5	140.1 ± 2.7	PE-NC-5-C	166.6 ± 3.2
PE-NCP(1)-0.1	156.3 ± 3.6	PE-NCP(1)-0.1-C	172.5 ± 5.9
PE-NCP(1)-1	113.4 ± 2.2	PE-NCP(1)-1-C	180.1 ± 3.7
PE-NCP(1)-5	132.3 ± 0.0	PE-NCP(1)-5-C	167.5 ± 4.4
PE-NCP(5)-0.1	109.7 ± 1.4	PE-NCP(5)-0.1-C	155.9 ± 2.5
PE-NCP(5)-1	115.6 ± 2.9	PE-NCP(5)-1-C	178.8 ± 4.4
PE-NCP(5)-5	120.5 ± 2.9	PE-NCP(5)-5-C	176.0 ± 5.3
PE-NCP(20)-0.1	121.2 ± 5.2	PE-NCP(20)-0.1-C	150.4 ± 0.4
PE-NCP(20)-1	134.0 ± 4.2	PE-NCP(20)-1-C	169.6 ± 3.6
PE-NCP(20)-5	133.4 ± 5.0	PE-NCP(20)-5-C	177.1 ± 5.8
PE-NCP(100)-0.1	123.4 ± 3.1	PE-NCP(100)-0.1-C	173.0 ± 4.4
PE-NCP(100)-1	160.5 ± 1.2	PE-NCP(100)-1-C	161.8 ± 2.5
PE-MB-0.1	150.7 ± 2.0		
PE-MB-1	152.3 ± 1.2		
PE-BU-0.1	162.6 ± 5.0		
PE-BU-1	165.8 ± 3.2		
PE-BU-5	177.5 ± 2.6		

due to the humidity content. For example, in Figure 5, the TG curves for the set PE–NCP(20) are represented. Other authors obtained similar results for the thermal stability of PE nanocomposites in inert atmospheres.^{1,29,30} Zhao et al.³⁰ suggested that the organoclay would have two opposing effects over the thermal stability of the PE nanocomposites: it could improve the thermal stability by acting as a barrier for diffusion and inhibiting the polymer decomposition, or it could catalyze the degradation of the polymer matrix. The thermal stability of the materials would increase or decrease, depending the dominant effect and thus depending on the sample morphology and the amount of organoclay.

The behavior of the samples containing MB and BU was also quite similar. Nevertheless, the thermal stability of the samples with the highest concentration was slightly lower at the earlier stages of the process, as shown in Figure 6 from 80°C on.

Bleeding

All of the prepared samples were subjected to standard migration tests (ASTM D 279-2). It was proven that there was no bleeding of the organic dye out of the PE matrix in any of the samples prepared with BU or NCP [Figure 7(a)]. However, there was bleeding of the dye in the samples prepared with MB (set PE–MB), as shown in Figure 7(b), where the plaques of PVC stained with the dye can be seen. Therefore, this indicates that NCPs could be appropriate colorants for certain applications, such as food contact, plastics, packaging, and toys.

Color Performance. Table VI shows the values of *D* and Φ for the PE samples colored with conventional colorants and NCP. It was observed that from a colorimetric point of view, the presence of the compatibilizer did not modify the color of the sample. Therefore, to assess the color performance of the nanopigments, only the samples without compatibilizer are shown.

Both *D* and Φ increased when the concentration of the colorant (pigment, dye, or nanopigment) in the sample and/or the percentage of MB exchanged in the NCP increased. When the NCP was compared to the organic dye, the samples colored with NCP(100) had values of *D* similar to the samples colored with MB, but the Φ values were higher in the samples with NCP(100) compared to those in the samples with MB. Nevertheless, it is worth mentioning that the actual percentage of dye in the NCP(100) pigment was around 20 wt %, whereas the rest was NC. Therefore, the amount of MB molecules that gave color to the samples with NCP(100/0) was about five times lower than that in the samples with only dye, whereas the color performance was equal or even higher than that in the samples with MB. One possible explanation for this behavior is that when the dye was added to the polymer, it was not entirely dissolved and formed aggregates. These MB aggregates, which could be identified at sight, reduced the number of dye molecules that interacted with the light to develop the color. Meanwhile, when the dye was acting as a surfactant in the clay, in part occupying interlayer positions or on the external surface of the NC, there was no possibility for MB to

Table V. Energy Absorbed at Break for PE with and Without Compatibilizer and with Nanoclay and Those Colored with NCP(X), MB, and BU

Sample	Energy absorbed at break (J)	Sample	Energy absorbed at break (J)
PE	20.3 ± 3.4	PE-C-0.3	22.0 ± 2.7
		PE-C-3	21.3 ± 4.5
		PE-C-15	14.2 ± 1.0
PE-NC-0.1	21.8 ± 2.1	PE-NC-0.1-C	24.2 ± 1.9
PE-NC-1	19.5 ± 1.4	PE-NC-1-C	21.3 ± 2.2
PE-NC-5	10.4 ± 3.1	PE-NC-5-C	15.0 ± 3.2
PE-NCP(1)-0.1	22.7 ± 2.4	PE-NCP(1)-0.1-C	20.8 ± 4.3
PE-NCP(1)-1	17.9 ± 2.4	PE-NCP(1)-1-C	25.3 ± 4.6
PE-NCP(1)-5	9.6 ± 2.2	PE-NCP(1)-5-C	15.4 ± 2.7
PE-NCP(5)-0.1	14.5 ± 2.1	PE-NCP(5)-0.1-C	17.0 ± 1.8
PE-NCP(5)-1	16.7 ± 1.3	PE-NCP(5)-1-C	20.8 ± 1.5
PE-NCP(5)-5	9.3 ± 0.3	PE-NCP(5)-5-C	15.9 ± 0.8
PE-NCP(20)-0.1	16.5 ± 1.5	PE-NCP(20)-0.1-C	15.5 ± 2.7
PE-NCP(20)-1	20.3 ± 1.4	PE-NCP(20)-1-C	24.2 ± 0.3
PE-NCP(20)-5	12.4 ± 1.3	PE-NCP(20)-5-C	21.3 ± 2.7
PE-NCP(100)-0.1	6.4 ± 3.0	PE-NCP(100)-0.1-C	15.0 ± 3.3
PE-NCP(100)-1	17.8 ± 1.7	PE-NCP(100)-1-C	20.8 ± 1.7
PE-MB-0.1	12.5 ± 1.6		
PE-MB-1	6.4 ± 4.6		
PE-BU-0.1	16.3 ± 1.8		
PE-BU-1	20.1 ± 1.4		
PE-BU-5	22.1 ± 2.4		

aggregate. Therefore, the MB molecules were separated in a way that they interacted more actively with light and developed color more effectively. In other words, with a low amount of dye acting as a surfactant, not only was the dispersion of the NC enhanced, but also a higher, intense color was obtained.

On the other hand, when the NCP was compared to the inorganic pigment, BU, we noticed that the NCPs with low loads of MB, NCP(1) and NCP(5), presented values of *D* similar to the inorganic pigment, whereas the NCPs with higher percentages

of CEC exchanged with MB, NCP(20) and NCP(100), had values that were higher than those for the inorganic pigment. The values of Φ of the samples with blue ultramarine were higher than those for the samples with NCP(1) and NCP(5); these were similar to the ones with NCP(20) and much lower than those with NCP(100). Therefore, because the load of colorant in the samples colored with the synthesized nanopigment was much lower than in the samples colored with MB or BU, it can be said that nanopigments were superior in color performance than these colorants.

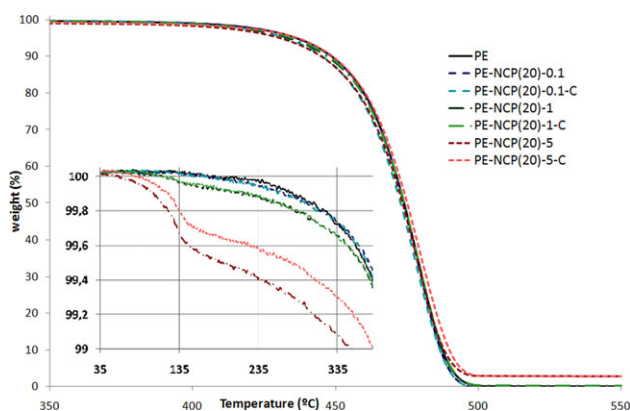


Figure 5. TG curves for the set of the set of the PE-NCP(20) samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

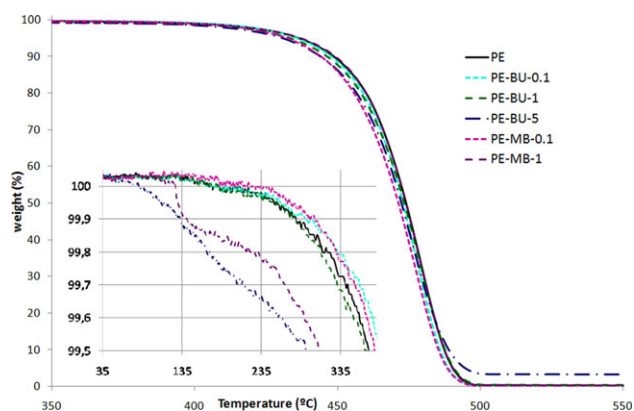


Figure 6. TG curves for the set of samples with BU and MB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Colorfastness

From the measures of the reflectance spectra, ΔE^*_{ab} and the difference in lightness (ΔL^*) and in Δa^* and Δb^* were calculated. For example, in Figure 8, the color variation as a function of the exposure time for the PE and PE–NCP(100)–0.1 samples is represented. In all cases, Δb^* was the one that contributed more to ΔE^*_{ab} , with a positive value; this means that the color of the sample shifted to yellow. That could have been a consequence of the oxidation of the polymer. Δa^* changed slightly, whereas ΔL^* was negative in the PE; this means that the sample was darker and slightly positive in PE–NCP(100)–0.1; this could have been due to the loss of some colorant. In general, all the sets of samples behaved in a similar way; the color variation followed an exponential trend, except for the samples with a higher concentration (5 phr), where there was a slightly linear variation of ΔE^*_{ab} with the exposure time. Δb^* was the one that contributed more to ΔE^*_{ab} in all of the samples.

We estimated that only values of ΔE^*_{ab} higher than 3 were noticeable by humans beings. For all of the sets of samples studied in this work, the darkest were under this value for the whole test, whereas the lightest reached these values at 100 h of exposition or even before. In Figure 9, For example, ΔE^*_{ab} as a function of the exposure time for PE–BU and PE–NCP(20)–C sets are shown. Both sets behaved similarly.

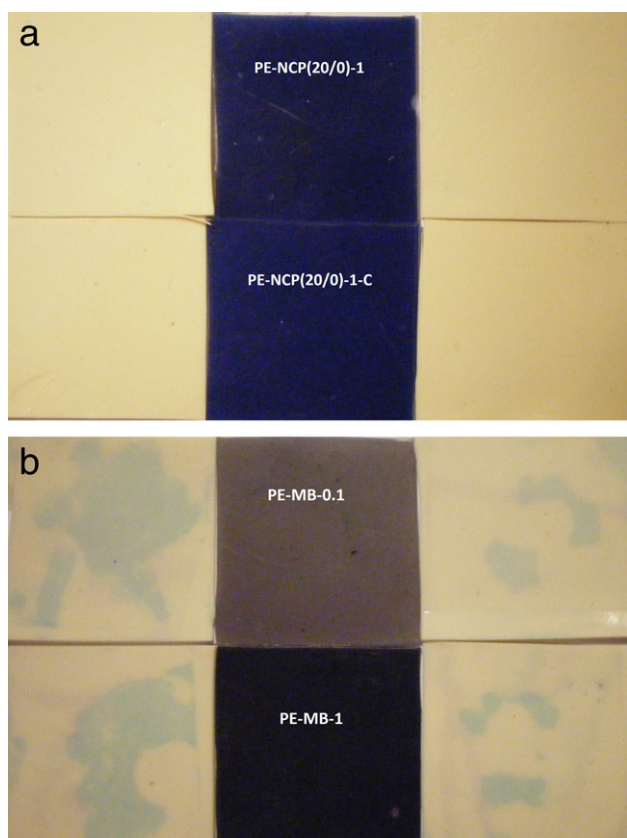


Figure 7. Plaques of PVC with 0.1% TiO₂ for the migration test of the samples: (a) PE–NCP(20)–1 and PE–NCP(20)–1–C and (b) PE–MB–0.1 and PE–MB–1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. D and Φ PHgr; Values for the Samples Without Compatibilizer

Sample	D (%)	Φ (m ² /mL)
PE-NC-0.1	15.4	0.042
PE-NC-1	14.3	0.042
PE-NC-5	20.3	0.076
PE-NCP(1)-0.1	15.4	0.045
PE-NCP(1)-1	17.0	0.053
PE-NCP(1)-5	41.6	0.343
PE-NCP(5)-0.1	18.2	0.053
PE-NCP(5)-1	21.3	0.079
PE-NCP(5)-5	51.0	0.290
PE-NCP(20)-0.1	20.2	0.059
PE-NCP(20)-1	29.2	0.179
PE-NCP(20)-5	78.7	0.563
PE-NCP(100)-0.1	25.4	0.195
PE-NCP(100)-1	86.7	0.617
PE-MB-0.1	26.6	0.162
PE-MB-1	81.4	0.537
PE-BU-0.1	19.5	0.072
PE-BU-1	24.6	0.324
PE-BU-5	37.3	0.646

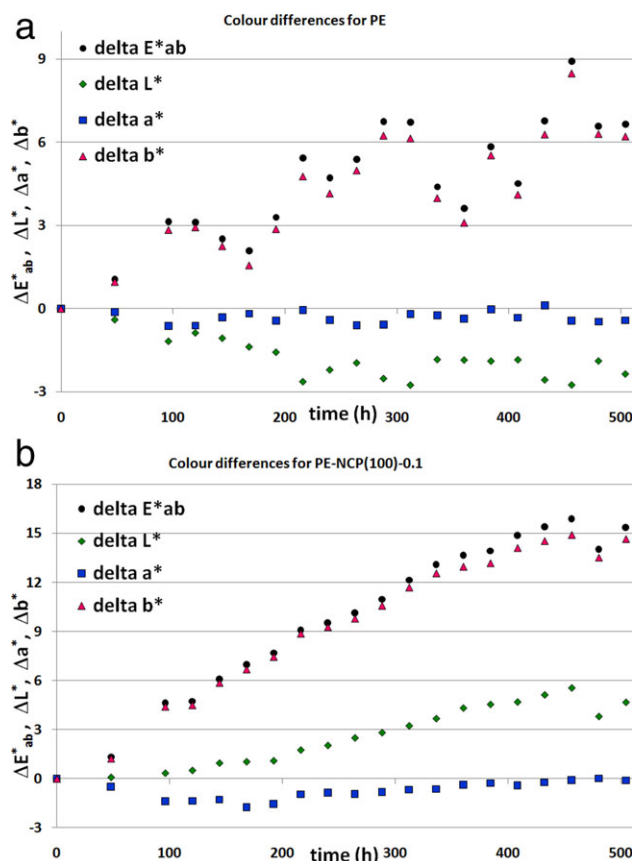


Figure 8. Color variation (ΔE^*_{ab} , ΔL^* , Δa^* , and Δb^*) as a function of the exposure time for the samples: (a) PE and (b) PE–NCP(100)–0.1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

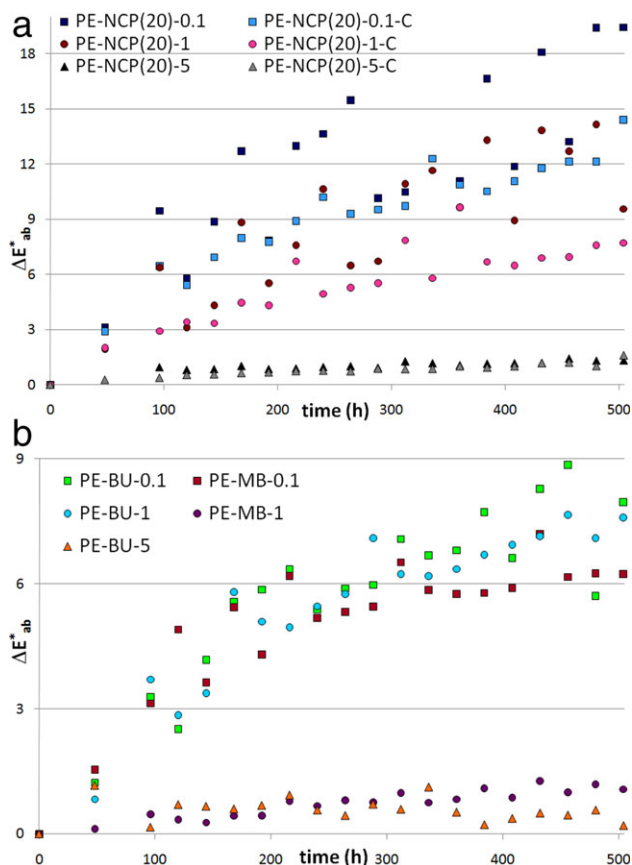


Figure 9. ΔE^*_{ab} as a function of the exposure time for the following set of samples: (a) PE–BU and PE–MB and (b) PE–NCP(20)–C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

CONCLUSIONS

A novel kind of hybrid pigment based on an NC (sodium montmorillonite) and a dye (MB), has been prepared at the laboratory. To obtain a gamut of colors, the percentage of the CEC of the NC exchanged with the dye was varied. Furthermore, the NC-based pigments (NCP) obtained were applied to LLDPE with different levels of loading in a melt intercalation process, and the mechanical, thermal, and colorimetric properties of the mixtures were assessed. We came to the following conclusions:

- The morphology of all of the samples was intercalated and the presence of the compatibilizer improved the dispersion of NCP in the sample.
- The mechanical properties of the samples could increase or even slightly decrease, depending on the load of NCP and the percentage of MB interchanged. In samples that included compatibilizer and synthesized NCP, E and E_{abs} increased up to 60%; this could have been due to the improvement in the dispersion of the nanoadditive.
- The presence of the nanopigment, with or without compatibilizer, in the samples did not noticeably affect the thermal stability of the PE.
- The color performance of the NCPs was superior to that of conventional colorants. With a much lower load of

colorant, it was possible to achieve similar or even higher values of D and Φ .

- There was bleeding of MB out of the PE only when the dye was incorporated (set PE–MB), whereas no bleeding was observed in samples colored with the synthesized NCPs.
- In the weather-aging test, the loss of color was more evident in the samples with low concentrations of additive, whereas in the more concentrated samples, ΔE^*_{ab} was lower, independently of the type of pigment employed. In all cases, the major ΔE^*_{ab} was due to a shift to yellow.

As a general conclusion, when the MB was supported in the clay, it acted as surfactant, aiding the clay dispersion into the polymer matrix, but in this way, MB aggregates were not produced. Consequently, the synthesized NCPs employed with PE offered similar or better mechanical and thermal properties than the conventional colorants and higher color and bleeding performance but at a much lower concentration of colorant.

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