Nanoclay-based Pigments: synthesis, characterization and application

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ABSTRACT

Nanoclay-based pigments are promising colorants. They enhance the colorimetric properties of the dye giving more intense and saturated colours. In addition, they act as reinforce additive when they are dispersed into polymers. They can be applied in a wide variety of substrates: printing inks, textiles, acrylic paints and concrete; and more applications are being developed. One important advantage of the nanoclay-based pigments is the fact that they can be considered an ecological alternative to contaminant colorants, in contrast to some traditional inorganic pigments that contend heavy metal in their structure.

INTRODUCTION

When colouring polymers, several factors must be taken into consideration, such as the compatibility between the polymer and the colorant, the stability of the colorant to the polymer processing conditions and the level of dispersion that can be able to achieve with the processing techniques. Moreover, the final application of the product affects the selection of the system (polymer and colorant). But also, the presence of other additives can affect the dispersion of the colorant in the polymer matrix and the final colour and/or appearance of the system. Generally, the colorants used for the colouration of polymers are organic and inorganic pigments and dyes. Each type of colorant has its advantages and drawbacks. Organic and Inorganic Pigments are insoluble in the polymer matrix and are difficult to disperse, but they offer a good hiding power. Dyes are soluble in the polymer matrix and offer a wide colour gamut and colour saturation, but they have low resistance against factors like UV radiation and temperature. In addition, migration of the dye out of the polymer matrix can occur (Charvat, 2005). Nevertheless, research in nanomaterials has addressed this issue to develop new colorant materials.

In the polymer nanocomposites field, the organically modified nanoclays have gained remarkable importance as nanoadditives because with low content they can confer great improvement in the polymer properties, like mechanical strength, thermal stability and barrier properties (Pavlidou and Papaspyrides, 2008; Zeng et al., 2005; Livi et al., 2010; Sinha Ray and Okamoto, 2003). Falling in this category, the nanoclay-based pigment (NCP) or nanopigments are organically modified nanoclay in which all or part of the cationic exchange capacity (CEC) of the nanoclay is exchanged with an organic dye and, in some cases, with organic surfactants, like quaternary ammonium. Originally the NCPs were developed by Batenburg and Fischer (2001) in the TPD-TNO (Eindhoven) and have been applied mainly for colouring polymers, in which they act as reinforcement filler and as a colorant. Initially, this hybrid materials were claimed to improve the properties of the polymeric matrix and also to gather the advantages of dyes and pigments, such as brilliant colours, wide colour gamut, while avoiding their drawbacks, like bleeding, low lightfastness, low stability against oxygen, temperature, UV radiation (Batenburg and Fischer, 2001). There is a great number of studies about the incorporation of dyes in clays and the properties of the clay-dye systems (Bergmann and O'Konski, 1963; Bujdák et al., 2007; Bujdák et al., 2003; Čapková et al., 2004; Gessner et al., 1994; Grauer et al., 1987; Klika et al., 2004; Landau et al., 2002; López Arbeloa et al., 2002; Monvisade and Siriphannon, 2009; Pospíšil et al., 2003; Tapia Estevez et al., 1993; Wang et al., 2004) and also, some studies have been carried out to assess the influence of the NCP in thermoplastic polymers (Raha et al., 2009; Marchante et al., 2012; Marchante et al., 2013b; Marchante et al., 2013a). Moreover, they can be used to produce coatings, paints or to colour other substrates. Others studies have been done to study the synthesis of this type of nanoclay-based pigments with different dyes (Raha et al., 2012; Sivathasan, 2007). Sivathasan (2007) observed a significant improvement on the thermal and UV stability of samples of polystyrene coloured with nanoclay-based pigments.

In this paper we present a review of the research conducted at the University of Alicante regarding this promising type of hybrid and ecological pigment.

SYNTHESIS

The synthesis of NCP at laboratory scale was first described by Batenburg and Fischer (2001) and it can be summarized as follows: Firstly, the nanoclay has to be dispersed preferably in deionized water, where it swells. This increases distance between clay sheets and, as a consequence, reduces ionic bond force of counterions of clay. After that, a dye solution is added to the dispersion. Then ionic exchange takes place and the dye molecules replace the counterions of the nanoclay. Next step is to filter the dispersion and dry the cake. It can be done through several techniques: freeze drying, spray drying or in a muffle. Figure 1 shows a flowchart of the process.

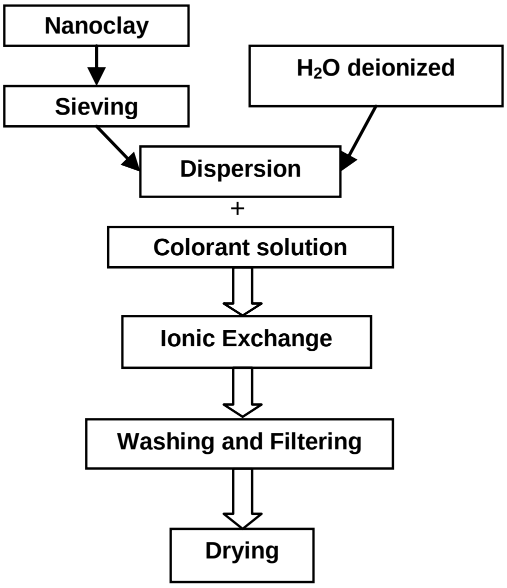


Figure 1.-Flowchart for the synthesis of NCP

However, This process can be optimised (Marchante Rodriguez, 2012). It has been produced NCP varying the percentage of CEC exchanged with dye and also exchanged the nanoclay with two surfactants, a dye and a quaternary ammonium salt (Marchante et al., 2013b; Marchante et al., 2013a) (Figure 2). As a result, it was obtained a NCP which showed enhanced colorimetric properties and better dispersion when it was applied in EVA copolymer.

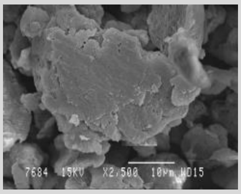
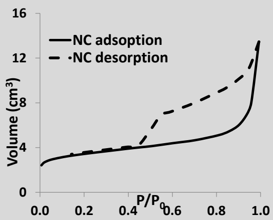
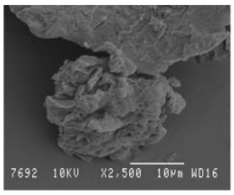
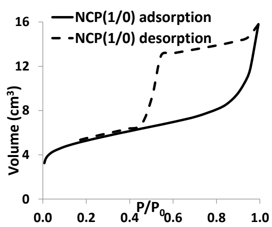
Figure 2.- Image of several NCP synthetized at the University of Alicante.

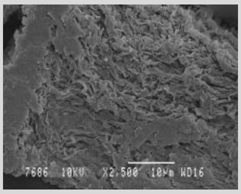
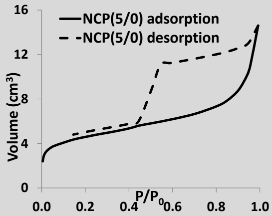
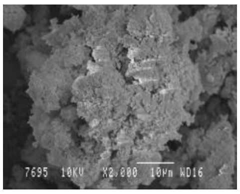
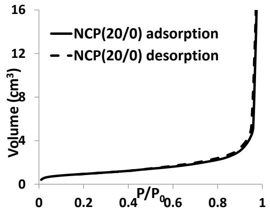
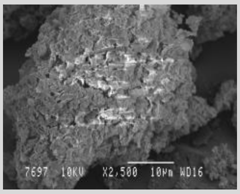
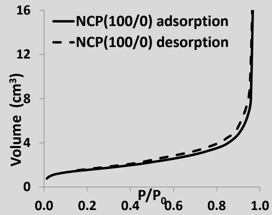
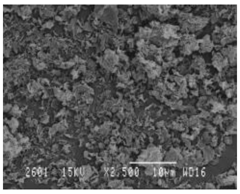
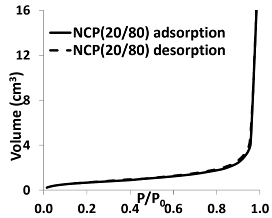
In some studies (Raha et al., 2012; Sivathasan, 2007), the NCPs have been synthesised using non-aqueous medium. Sivanthasan (2007) synthesised nanoclay-based pigments using two methods, one using unmodified clay (sodium montmorillonite) in aqueous medium, and other with organically modified clay (Cloisite 15A) in non-aqueous medium. The non-aqueous medium method is similar to the aqueous one, but in this case the organically modified clay was dispersed in a solvent, (dichloromethane), and then the dye and a protonation agent (perchloric acid) was added to the dispersion. On the other hand, Raha et al. (2012) synthesised NCPs from non-ionic dyes. They modified the dyes and obtained the corresponding tertiary amines using an alkylating agent, and then they treated the amines to get the salts. After that, the NCP was obtained by ionic exchange of the modified dyes and the nanoclay (sodium montmorillonite) in an acidic medium.

PROPERTIES OF SYNTHESISED NANOCLAY-BASED PIGMENTS

Table 1 shows several properties of the nanoclay (NC), specifically a sodium montmorillonite, and several nanoclay-based pigments (NCP) synthesized at the University of Alicante. These NCP were obtained from exchanging the Na^+ cations of the nanoclay (Nanofil®116, Süd Chemie) with a dye (methylene blue, MB,Sigma-Aldrich) and a quaternary ammonium salt (S) (ethyl hexadecyl dimethyl ammonium bromide, Sigma-Aldrich). The CEC percentage exchanged with the dye was 1, 5, 20 and 100%, thus the NCP were named NCP (1/0), NCP(5/0), NCP(20/0) and NCP(100/0) respectively, and in NCP(20/80) the NC was exchanged a 20% of CEC with the dye and a 80% with the quaternary ammonium salt (Marchante et al., 2013b; Marchante et al., 2013a).

Table 1.- Characterization of a nanoclay (NC) and several nanoclay-based pigments (NCP).

	SEM	XRD (2θ)	Interlayer distance	Surface area	N_2 adsorption
NC		6.9º	2.9 Å	79.2 m^2/g	
NCP(1/0)		5.8º	5.3 Å	75.6 m^2/g	

NCP(5/0)		5.8º	5.2 Å	61.8 m^2/g	
NCP(20/0)		4.5º	9.6 Å	43.7 m^2/g	
NCP(100/0)		5.2º	7.0 Å	46.8 m^2/g	
NCP(20/80)		4.1º	11.8 Å	40.5 m^2/g	

Morphology

Generally the modification in the morphology of nanomaterials and nanocomposites is studied with X-ray diffraction (XRD) and with transmission (TEM) and scanning electron microscopy (SEM). In the case of the NCP, the replacement of the counter-ion of the nanoclay for dye and/or surfactant molecules causes a displacement of the XRD peak to lower angles. This implies an increase in the interlayer distance in the nanoclay particles. As the content of MB and/or S in the NCP increases, the interlayer distance increases too. However, NCP(20/0) shows greater interlayer distance that NCP(100/0). This can be due to the hydration of the sodium cations (Xi et al., 2007; Marchante et al., 2013a). The change in the structure of NC particles can be observed in the SEM images: it passes from compacted clay sheets in NC to smaller particles in NCP(100/0) and NCP(20/80).

Surface modification

The presence of surfactants affects to other properties of the NC. The results of nitrogen absorption test of the NC and NCP (Marchante Rodriguez, 2012) show that there is a reduction in the surface area as the content of surfactant (dye and/or ammonium salt) increases in the NCP (table 1). In addition, nanoclay (NC) and low saturated nanoclay-based pigments (NCP(1/0) and NCP(5/0)) present an isotherm type IV with hysteresis cycle, while high saturated nanoclay-based pigments (NCP(20/0), NCP(100/0) and NCP(20/80)) present an isotherm type II. The presence of MB and S in the high saturated NCP could block the penetration of N_2 molecules in the pores of the NC and/or between the nanoclay layers. Wang et al. (2004) studied the absorption of basic dyes onto two types of montmorillonite, a non-modified calcium montmorillonite and a calcium montmorillonite exchange with titanium cations. They suggested that, for a particular type of clay, the reduction of the BET surface area was a consequence of two mechanisms, a surface screen effect due to the large size of the organic molecules and a pore blocking effect. In the case of the NCPs, both effects can act to reduce the surface area.

Thermal stability

When the dye and/or surfactant molecules are attached to the clay in the NCP it can be observed an improvement in the thermal stability of the dye and surfactant. For example, the DTG curves of the nanoclay-based pigment NCP(20/80) and its components, rated according to the percentage they are presented in NCP(20/80), (Figure 3) reveal that the weight losses of S and M are divided during the whole process and the peaks that correspond to the degradation temperatures of S and M are displaced towards higher temperatures.

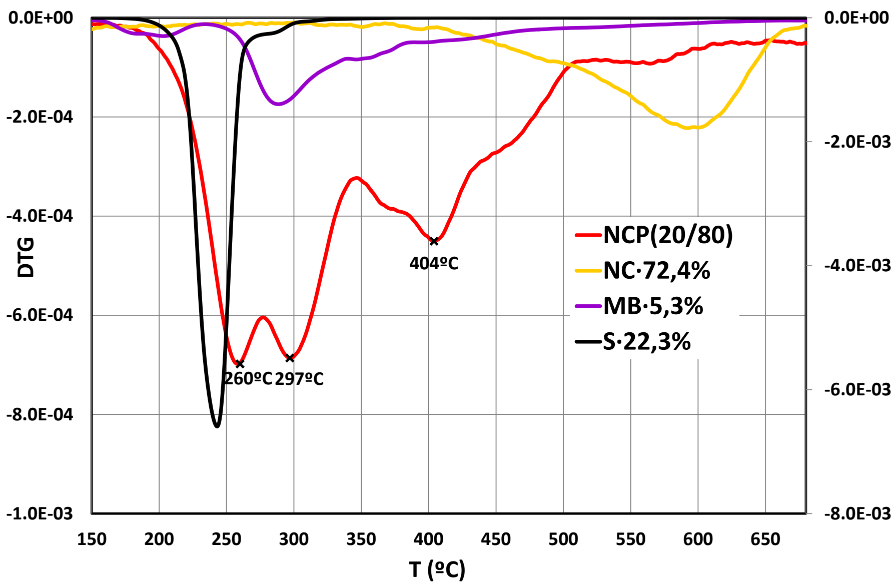


Figure 3.- DTG of NCP(20/8) and NC, MB and S, rated according to their content in NCP(20/80) (The DTG curve of S is represented in the secondary axis, on the right side) (Marchante Rodriguez, 2012).

APPLICATION

Initially the nanoclay-based pigments were developed to be incorporated into polymers: for making coating (Batenburg and Fischer, 2001) or for mass coloration (Fischer, 2003). The NCPs have been proved to be suitable colorants for polymers and also to act as reinforce additives (Marchante et al., 2012)(Marchante et al., 2013b)(Marchante et al., 2013a). The NCP above mentioned were used to prepare polymer/NCP composite. Three thermoplastic polymers with different polarity were employed: linear low density polyethylene (PE), ethylene vinyl acetate (EVA) and polyvinyl chloride (PVC). Only with PE was necessary to add a compatibiliser to improve the dispersion of the NCP. In general, the presence of the NCP did not affect significantly some properties like thermal stability or rheology (it is observed an increase in the dynamic and extensional viscosity only in the samples with high content of NCP and good exfoliation). Regarding the mechanical strength, the NCP improve the Young's moduli and but the ductility of the polymers decreases. On the other hand, the most remarkably results are obtained from the colorimetric aspect. Polymers coloured with NCP develop more intense and saturated colours than the samples coloured with the same dye used to synthetized the NCP. The content of dye in the samples coloured with the nanoclay-based pigment is about 5 times lower than the content of dye in the samples coloured with dye or conventional inorganic pigment. However, the values of colour performance parameters (hiding power and colouring power) are similar or in some case even greater. In addition, the colourfastness of the NCP/polymer composite increased and there was no migration of the NCP out of the polymer matrix (Marchante Rodriguez, 2012). These good properties position the NCP as a more ecological alternative to traditional pigments that contain heavy metal in their composition and are highly contaminant.

However, the application of NCP is not restricted to polymers. There are several examples of application of this type of nanopigment in different substrates. Some research has been conducted to use them in the formulation of printing inks for offset printing technology. The NCP were suitable to use as raw materialsfor offset printing inks, though their shade was not exactly the shade requested in the standard and, because of the limitation in in the amount of NCP added, it was not possible to achieve the requested colour saturation. Nevertheless, this problems can be solved by improving the dispersion of the NCP by adding surfactants or changing the dispersion process, combining several NCP and/or choosing the more suitable dye to be exchanged in the nanoclay (Marchante et al., 2009).

Another example of application of NCP is in acrylic paints. Two nanoclay-based pigments, a magenta NCP made of Rhodamine-6G (Sigma-Aldrich) and a blue NCP made of methylene blue (Sigma-Aldrich), both supported in montomorillonite Nanofil® 116 (Süd Chemie), were used in the paints (Figure 4). The formulation of these paints is listed in Table 2. Bleeding and UV resistance of these paints were tested. UV resistance was tested in a Xenon Test Chamber Model Xe-1-B Q-SUN with irradiance of 0.68 W/m^2 at 340 nm and 70 ºC for 48 hours. The samples for the bleeding test were prepared by spreading a layer of paint with a 4 k-bar over black and white cardboard cards and the bleeding test was carried out by spraying a white gloss aerosol sprayed over the samples. The blue paint showed no bleeding and had good UV resistance, while it was necessary to add a binder to the magenta paint in order to avoid the bleeding and also its UV resistance was lower than the blue paint.

Figure 4.- Paints formulated with NCP (University of Alicante) and 'Neutral Base' (HMG Paints Ltd.).

Table 2.- Composition of the paints formulated with NCP.

	Magenta paint	Blue paint
Neutral Base (HMG Paints)	75 g	150 g
H_2O deionized	25 g	50 g
Nano-clay based pigment	2 g	3 g
Dispersant (760 W, Degussa)	0,5 g.	None
Ball mill mixer	10 h	7 h

In addition, the application of the nanoclay-based pigments could be extended to other fields, like textiles or construction. Organically modified nanoclays (OMC) mixed with polymers can be applied into textile. There are mainly two routes to incorporate the OMC/polymer composites into textiles: the first way is by melt spinning the OMC/polymer composites and the textiles into yarns and then knitting them to make the fabric. And other possibility is coating the textile fabric with the OMC/polymer composites. when they are mixed with fabric are able to be applied into textiles (Ghosh, 2011). In the construction field, there are attempts to apply nanopigments to make a fluorescent type of concrete to be used in roads with a wide colour gamut and high colourfastness (AIDICO, 2012).

CONCLUSIONS

Nanoclay-based pigments are hybrid materials made of the combination of nanoclay particles and dyes. The dye molecules are attached to the nanoclay particles by ionic bonds. Thus some physical and chemical properties of the dye, such as thermal and UV stability are enhanced. In addition, supporting the dye on the nanoclay remarkably improves the colorimetric properties of the dye. Therefore, the nanoclay-based pigments can be used not only as powerful colorants, but also they can act as reinforce additive when they are dispersed into polymers. Another advantage of the NCP is the fact that they do not contain heavy metals in its composition and can be consider as an ecological alternative to some contaminant colorants.

At present, the application of these promising nanopigments in different fields (printing, textiles, acrylic paints, construction, etc.) is being developed and spread. Good results have been obtained when applied to acrylic paints and printing inks, though some problems, like achieving a good dispersion level or matching a specific hue, have to be solved and need further research. Moreover, in order to boost the commercialisation of the NCP a challenge to deal with is the development of a synthesis process at large scale.

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