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Effect of nanoclay on the dyeing ability of PA6 nanocomposite fibers

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Abstract

PA6 clay fibers were prepared by melt spinning. The experiments carried out in DSC showed that the presence of clay in PA6 induces the crystallization of PA6 in γ-form, increasing the crystallization temperature and decreasing the melting point. By measuring the melting enthalpy, we also noticed that the quantity of amorphous regions is higher in filled PA6 yarns. The accessibility of the filled fiber is thus improved. After dyeing experiments, we noticed that PA6 nano yarn dyes itself faster with disperse dyes than unfilled PA6 yarn, while it is the opposite with acid dyes and 2:1 metal complex dyes. In both latter cases the nanoclay fixes on the amino sites, preventing the fixation of the acid or metal complex dyes.

Keywords: Dyeing ability; Nanoclay; Polyamide-6 fibers; Nylon

1. Introduction

The polyamide-6/clay nanocomposite is one of the most extensively investigated nanocomposite polymers. In comparison with the unfilled polyamide-6 (PA6), the PA6/clay composite exhibits higher tensile strength, higher elastic modulus, improved heat resistance as well as excellent gas and water barrier properties [1–3]. Recently, its use as char forming agent in intumescent formulations was reported [4].

Because of its importance as a commercial synthetic fiber, many papers dealt with the melt spinning of PA6. The fiber structure formation was affected by the take-up velocity, the conditioning after spinning and the molecular weight of PA6 [5–9]. Nevertheless, only a few investigations of the melt or solution spinning of polyamide nanocomposite are available [10,11]. Giza and co-workers [10] prepared PA6/clay fibers by melt spinning at different take-up velocities and reported the influence of take-up speeds on the fiber structure. Vaia and co-workers [11] prepared such fibers by dissolution and reprocessing of exfoliated montmorillonite − PA6 nanocomposite. They noticed that the electrospinning process used resulted in highly aligned clay layers and an increase in crystallinity rate.

In a previous study [12], we described the crystallization behaviour of PA6 nanocomposite, synthesized by melt blending at high shear stress. We showed that the crystallinity of the PA6 nanocomposite was lower than that of the unfilled PA6. It implies a higher quantity of amorphous regions, which favours the dyeing of fibers. In the field of dyeing, only a few results about the dyeing of polypropylene nanocomposite are described in literature [13,14], none about the dyeing of PA6 nano.

We thus prepared PA6 and PA6 nano fibers under the same conditions. After characterizing them by

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differential scanning calorimetry, to be sure that the effect of the clay was still present after the spinning, we studied and analysed their behaviour on dyeing with three different dyes.

2. Experimental

2.1. Materials

Raw materials used for the preparation of polyamide-6 clay hybrids (PA6 nano) were sodium montmorillonite modified by methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride supplied by Southern Clay Product (Cloisite 30B) and polyamide-6 (PA6) as pellets supplied by Rhodia (Technyl C206). Clay and PA6 were dried 48 h at 80 °C before extrusion.

We used three dyes of different classes, used usually in the dyeing of polyamide. They are an acid dye, a 2:1 metal complex dye and a disperse dye. These dyes were obtained from Clariant and their chemical structure is reported in Table 1.

2.2. Preparation procedure of nanocomposite

2.2.1. Polyamide-6 clay hybrid nanocomposite

Polymer melt-direct intercalation is an approach to make polymer layered silicate nanocomposites by using a conventional polymer extrusion process. PA6 was melt-mixed with the clay (5 wt.%) using a corotative twin-screw extruder (type Rheomex PTW-16/25p from Thermo Haake) under conditions that permit the formation of nano-structured material [15]. The rotational speed was 300 rpm in order to have high shear stress and the temperatures of the five heating zones were 250 °C. The extrudate was then pelletised. This material was characterized in a previous paper [12]. It was shown that a well exfoliated PA6 nanocomposite was made without detectable degradation of the clay or the polymer.

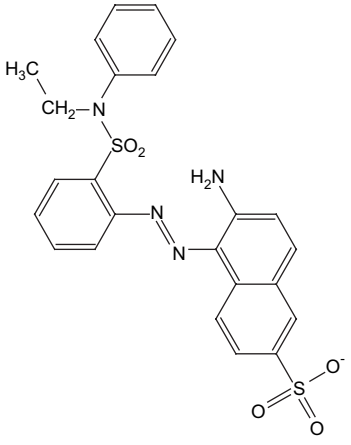
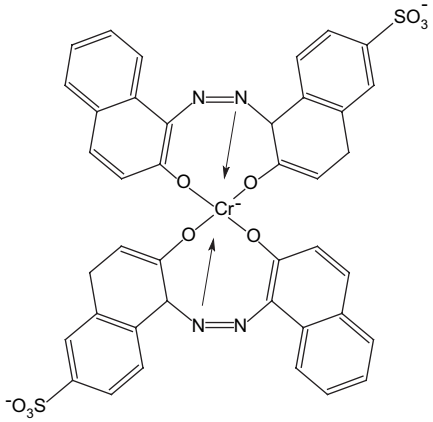
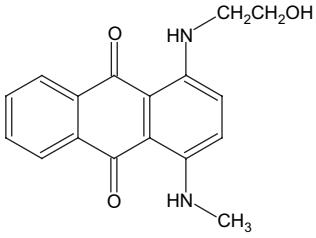
2.2.2. Polyamide-6 clay hybrid nanocomposite multifilament yarns

Multifilament yarns were made via a spinning process using a Busschaert Spinboy I melt spinning machine. The solid polymeric pellets were introduced in the spinning apparatus consisting of a single-screw extrusion system. In order to process the polyamide-6/clay hybrid nanocomposite yarns, the heating of the screw is regulated between 235 and 240 °C. A volumetric pump ensures the injection of molten polymer into the dye with a flow of 100 cm^3/min. The molten filaments are air cooled, covered with a textile coating, and then drawn by means of two heated rolls before being wound. The first roll has a surface speed of 200 turns/min and is heated at 80 °C, whereas the second turns at 550 turns/min and is heated at 100 °C. The final winding speed is the same as that of the second drawing roll. The yarns obtained consist of 80 trilobal continuous filaments of approximately 2000 dtex.

2.3. Dyeing conditions

The yarns were scoured prior to dyeing. The spin finishes used were water-dispersible and were eliminated with a boiling water treatment over 30 min. The spin finish elimination was controlled with dichloromethane being removed using a Soxhlet apparatus. Dyeing

Table 1
Chemical structure of the studied dyes

Dye No. 1: acid dye Nylosan Red E-BL CI Acid Red 57 No. 17503	Dye No. 2: 2:1 metal complex dye Lanasyn Navy Blue SD-NL CI Acid Blue 193 No. 15707	Dye No. 3: disperse dye Artisil BlueBSQ CI Disperse Blue 3 No. 61505
		

experiments were carried out with an Ahiba apparatus with a liquor ratio of 1:100. The dyebath used for the acid dye consisted of a CH_3COOH/CH_3COONa buffer to maintain a pH of 5, that for the 2:1 metal complex dye consisted of CH_3COOH/CH_3COONH_4 buffer to ensure a pH value of 6, and that for the disperse dye contained only CH_3COOH to maintain a pH of 5. The yarns were introduced into the dyebath at 40 °C and the temperature was then increased to 95–100 °C at a rate of 2 °C/min. After 60 min at this temperature the dyebath was cooled back to room temperature.

Two tinctorial studies were carried out: a kinetic study and an investigation on the equilibrium state.

2.3.1. Kinetic study

We worked with a dye concentration of 2% owf (over weight fiber). At the end of dyeing, the dyebath was recovered for colorimetric measurement in order to determine the quantity of non-fixed dye. We measured the exhaustion of the bath every 10 min during the increase of temperature and every 20 min on the plateau. These measurements were carried out with a spectrophotometer (type V530—Jasco).

2.3.2. Study of the equilibrium state

This study was carried out at 95–100 °C for 60 min with various dye concentrations from 0.5 to 3% owf. At the end of the dyeing, the samples were rinsed and the dyebaths and all the rinsing baths were recovered for colorimetric measurement. We calculated the concentration of the dye staying in the bath (C_b) as well as that in the fiber (C_f). We then drew the curves which illustrate the sharing of the dye between the bath and the fiber at the equilibrium state: $C_f = f(C_b)$.

2.4. Characterization

2.4.1. Differential scanning calorimetry

Differential scanning calorimetry was carried out under nitrogen flow on a 2920 modulated DSC from TA Instruments in pierced aluminium pan (about 10 mg sample) from 20 to 240 °C. The heating rate was 15 °C/min and the cooling rate was controlled at 15 °C/min. In order to measure the energies of melting, indium standard was used.

2.4.2. Washing fastness tests

Washing fastness tests were performed at 40 °C using the standard test for colour fastness (ISO 105-C01: 1989) on the two yarns (PA6 and PA6 nano dyed).

Three cotations are realised: the shade change/the staining on polyamide/the staining on viscose. The value scale is from 1 to 5. The value 5 signifies a very good fastness.

3. Results and discussion

3.1. Characterization

The fibers of PA6 and PA6 nano were characterized by DSC. Fibers were quickly heated to 240 °C under nitrogen, then maintained at this temperature for 3 min in order to destroy their thermal history related to the processing and to the shear stresses generated during extrusion. The samples were then cooled from the molten state to room temperature at a controlled cooling rate of 15 °C/min and without application of mechanical stresses on the material. Fig. 1 shows the crystallization curves observed during cooling. The exotherms maxima are located at 183 and 188 °C for the PA6 and PA6 nano yarns, respectively. The crystallization peak is shifted towards the high temperatures, when incorporating nanoclay. This phenomenon has already been described in the literature [12]. The nanoclay is then considered as a nucleating agent.

After cooling, the unfilled and filled PA yarns were melt with a heating rate of 15 °C/min. The melting endotherms are reported in Fig. 1. A large endothermic peak appears at 222 °C for PA6. PA6 is a semicrystalline polymer which crystallizes in a monoclinic form α, whose melting point is around 220 °C [16]. After crystallization of the filled yarns under the same cooling conditions, the endothermic peak is shifted towards the low temperatures, with a maximum around 215 °C. As described previously [12], this is due to the development of the γ crystalline form of PA6, induced by the presence of the clay.

A melting enthalpy of approximately −68.2 J/g is measured in the case of PA6 yarns, whereas it reaches −59.0 J/g for the filled yarns. This result was already

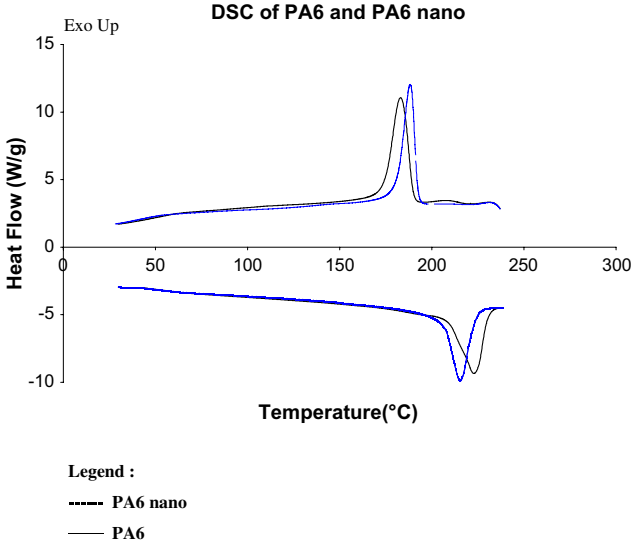


Fig. 1. DSC curves.

noticed in a previous work [12]. It shows that the crystallization rate of the nanocomposite material is lower than that of the PA6 alone. The quantity of amorphous regions is then higher in PA6 nano yarns. This could then induce a different dyeing behaviour.

3.2. Dyeing studies

The dyeing behaviour of a fiber depends on both its physical and chemical structures. For the former, the fiber structure must be accessible to water, dyes and other reagents. It must have a certain permeability to permit, particularly, the dye molecules to diffuse into the fiber matrix. In addition, fiber structure should be able to swell in water and also in the dyebath to facilitate this dye diffusion. It is presumed that dye molecules can diffuse only in non-crystalline regions of the fiber [17–19]. Treatments or processes like heat setting or drawing produce fiber modifications in its amorphous regions, and this has influence in the rate of dye-uptake [20]. For the latter, dyeability is governed by the presence, firstly, of polar groups which interact with water molecules and allow fiber swelling, and secondly, of reactive groups which attract dye molecules [17–19].

PA6 fibers can be represented by HO–[CO–$(CH_2)_5$–NH]$_n$–H or HOOC–R_n–NH_2. Because of their chemical composition and their production process, in polyamide fibers like many synthetic fibers, macromolecular chains are highly oriented so that amorphous regions are very small. Functional groups in PA6 are –NH_2, –COOH and –CO–NH–. Their numbers and their accessibility are limited, so that their water absorptivity is very low: PA6 moisture regain has values between 3.5 and 5% at 65% H.R. and 21 °C and PA6 swelling is about 2% [19].

In other respects, polyamide fibers present both hydrophilic character, conferred by –NH_2, –COOH and –CO–NH–, and hydrophobic character conferred by –$(CH_2)_5$– [17,18]. In general, hydrophilic fibers swell appreciably in water and are able to accept water-soluble ionic dyes, and hydrophobic fibers show little or negligible swelling in water and are permeable only to non-ionic dyes of low solubility [19]. The presence of amine end-groups gives polyamide fiber substantivity towards anionic dyes like acid dyes or metal complex dyes. The hydrophobic character of polyamides also makes their dyeing possible with disperse dyes which are non-ionic. Other dye classes can be used when polyamide chemical structure is modified [21].

We thus realised the dyeing of the PA6 nano and PA6 yarns with three dyes of different classes. The results obtained during the kinetic study are illustrated in Fig. 2 (a–c). These results show that PA6 dyes itself faster than PA6 nano with the acid and metal complex dyes, while it is the opposite for the disperse dye. The study of the equilibrate state leads to the same results

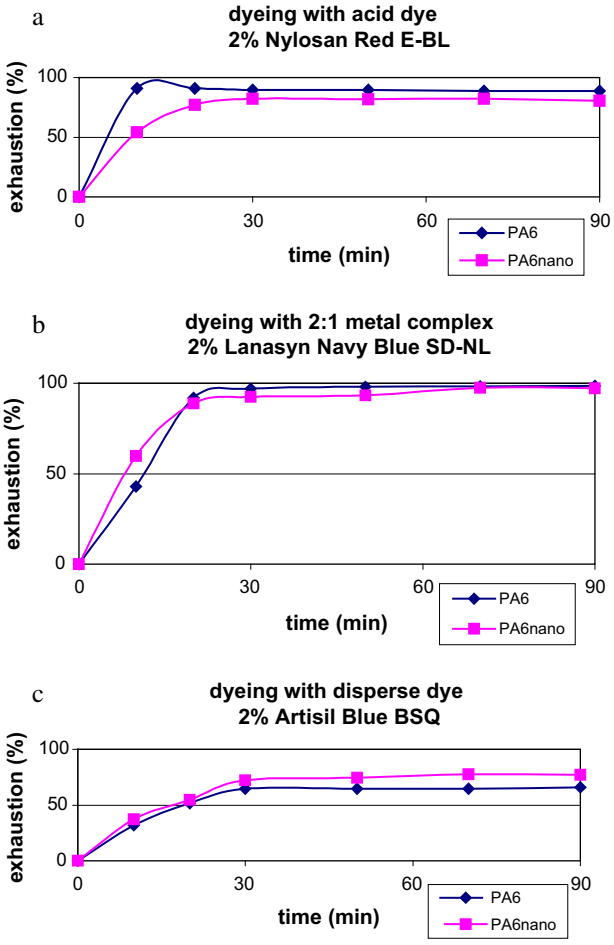


Fig. 2. Kinetic study of the dyeing of PA6 and PA6 nano. (a) Acid dye, (b) 2:1 metal complex dye and (c) disperse dye.

(Fig. 3a–c). Indeed, for the same concentration of dye at the beginning, PA6 fixes more acid dye and metal complex dye than PA6 nano to the equilibrium, while it is the opposite with the disperse dye. We can explain it in the following way.

The acid and metal complex dyes, due to their ionicity, fixed on the –NH_2 sites of the polyamide, which become NH_3^+ in acidic medium. Usuki and co-workers [1] suggested that the ammonium cations in PA6 interact with the anions in montmorillonite. The nanoclay blocks these –NH_2 sites and this phenomenon prevents the acid and metal complex dyes from fixing more on the PA6 nano.

On the other hand, the disperse dye solubilises in the PA fiber by, in particular, hydrophobic interactions. Cloisite 30B would also have hydrophobic character which would allow to attract more disperse dye, in the nanocompound. Besides, the accessibility of the fiber would be improved by the introduction of particles and it could then absorb more dye. This was also described in the case of the dyeing of nano-polypropylene [13]. According to Fan and co-workers, the dyeing was possible thanks to the tortuous pathways created by

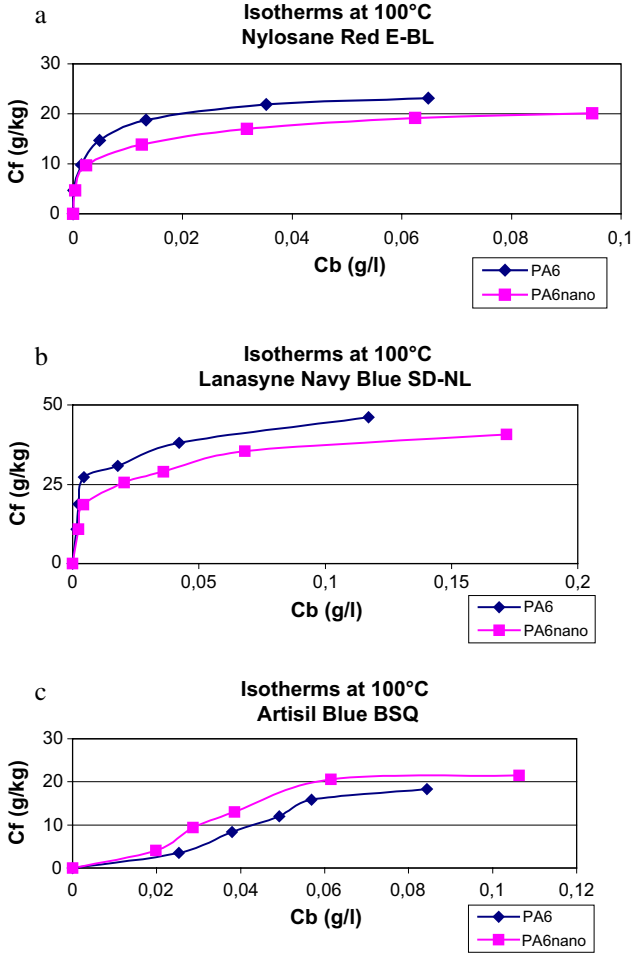


Fig. 3. Dyeing at equilibrium. (a) Acid dye, (b) 2:1 metal complex dye and (c) disperse dye.

oriented nanoclay layers in the polymer system, then modifying the accessibility of the fiber.

3.3. Washing fastness

The washing fastness test results are shown in Table 2. Globally, the introduction of nanoclay in the polyamide does not affect the fixation of dyes. The fact that, on one hand, the washing fastness is the same, and that on the other hand, the looks of isotherms are the same for every class of dyes on the two yarns leads us to say that the modes of fixation of the three studied classes of dyes are the same and that mechanisms involved during these fixations remain unchanged.

Table 2
Washing fastness results at 40 °C in terms of shade change/staining on polyamide/staining on viscose

Dye	PA6	PA6 nano
No. 1	5/5/5	5/5/5
No. 2	5/5/5	4–5/5/5
No. 3	4–5/5/5	4–5/5/5

4. Conclusion

Multifilament yarns of PA6 and PA6 nanocomposite were made via a melt spinning process. They were characterized by DSC. The results obtained confirm what we obtained for the corresponding polymers. The introduction of nanoclay induces a higher crystallization temperature and a lower melting point. The crystallinity of the PA6 nanocomposite yarn is lower than that of the unfilled PA6. The introduction of the nanoclay improves the accessibility of the fiber and this favours the dyeing of the PA6 nano with disperse dye. Nevertheless, because of the interactions between the anions in montmorillonite and the amino groups on the fiber, the dyeing sites are occupied with the nanoclay. This leads to a worse dyeing with the acid or the 2:1 metal complex dyes than in the case of the unfilled yarn.

Thanks to the thermodynamic studies and the washing fastness test, we proved that the mechanisms involved during the fixation of the dyes are unchanged by the introduction of the nanoclay.

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