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Material Behaviour

Strategy to improve PA6 performances by melt compounding

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ABSTRACT

PA6 is widely used for packaging and engineering applications. Literature reports that organically modified nanoclays can improve its flame resistance, thermo-mechanical and gas barrier properties. This study aims at showing a new approach to effectively disperse an unmodified nanoclay (MMT) in PA6 by melt compounding polymeric matrix and clay in the presence of dipentaerythritol (DPE). The prepared composites have been studied in terms of composition and thermal characteristics; moreover, by using a combination of wide and small angle X-ray diffraction data and transmission electron microscopy observations it has been possible to draw the conclusion that a good dispersion of MMT platelets is obtained. The reason has been imputed to probable interactions between DPE, PA6 and clay. On the other hand, the nanoclay can prevent the DPE separation by crystallization. This synergistic effect between DPE and MMT has been observed for balanced amounts of additive and clay. Final properties, in particular barrier properties, are notably enhanced.

1. Introduction

PA6 is a widely used resin, characterized by a unique combination of properties, such as mechanical strength, low coefficient of friction, transparency, thermoformability, high resistance to a wide spectrum of fuels, oils, and chemicals [1]. For these properties, PA6 found numerous applications, such as in the production of flexible packaging films, in most cases combined with polyolefins as a component of a multilayer structure.

However, despite a favourable set of properties, performances of PA6, mainly in terms of mechanical properties, flame retardancy, and low permeability to gases, could be significantly improved [2]. The scientific and patent literature reports various attempts to boost the above-mentioned properties by adding nanofillers into the polymeric matrix. A widely studied strategy is based on the use of small amounts of organically modified nanoclays, which are dispersed into the matrix through different methods, such as in situ polymerization [3], electrospinning [1], melt compounding [4–8].

While the most successful preparation technique was identified in polymerizing caprolactam in the presence of organo-modified montmorillonite, the resulting materials has found limited applications.

Indeed, even if the use of organo modified clays allows the preparation of well -dispersed nanocomposites, ensuring often an enhancement of barrier properties [5,6,9], several problems and limitations prevented a broad adoption of this approach. The increased complexity and logistics, tied to the production of PA6 nanocomposites in a typical polymerization plant, resulted in costs that not always can compete with alternative polymers. Moreover, the limited thermal resistance of organo modifiers such as ammonium and phosphonium salts almost invariably leads to degradation during processing and generation of by-products. Also, intercalating agents can migrate out the nanocomposite during shelf life. In short, costs, thermal stability issues, safety concerns, off flavor, due to chemical release, have largely limited the applications of melt compounded nanocomposites to non-food industries, such as automobile and electrical composites [10,11].

On the other hand, attempts to disperse non-modified clays in polyamides during extrusion generally do not provide nanoscale dispersion of the platelets [10].

In order to address such issues, the present study aims at showing that, under certain conditions, melt compounding can be an extremely effective technique for preparing dispersions of unmodified montmorillonite in polyamide by simple extrusion in the presence of a thermally stable co-ingredient.

Indeed, it is possible to plan a strategy that uses an additive rich in OH-groups that can interact with both the polymeric matrix and the clay, inducing not only macromolecular interconnections but also improving the intercalation of the nanoclays. Therefore, in the final nanocomposites the new macromolecular network and the good clay dispersion could show synergistic effects to improve certain performances of the material, for example in terms of barrier properties.

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The use of low molecular weight additives, rich in functional groups, which favour links between macromolecular chains and, then, cause a decrement of the chain mobility, has been studied by our group on EVOH matrix [12]. Moreover, Peter et al. [13] blended EVOH matrix and N,N′-bis(2,2,6,6-tetramethyl- 4-piperidyl)- isophthalamide (Nylostab SEED), in amounts lower than 2.0 wt%, and obtained an increment of oxygen barrier properties. This effect stems from interactions between hydroxyl groups of the polymer and amide units of the additive. It is worth noting that this occurs when the additive dissolves in the amorphous phase of the polymer, i.e. only with a very low percentage of additive; otherwise, a phase separation of the additive, at higher concentration, induces a deterioration of properties.

In this context, DPE can be an interesting molecule because it is rich in OH groups and can therefore strongly interact with PA6 matrix inducing a high density of hydrogen bonds. Moreover, DPE is safe for use in certain food contact related applications, it is obtained from renewable resources and it is characterized by low volatility and excellent heat and oxidation stability. It has also been reported that DPE can also improve PA thermal stability [14]. Finally, it is remarkable that DPE and certain of its derivatives have a good interaction also with nanoclay. For instance, a MMT clay modified with pentaerytrytol stearate can be easily exfoliated in PA6 nanocomposites [11]. DPE is also a component, together with nanoclays, in some formulations in intumescent fire retardant (IFR) coatings [15–17].

A synergistic effect between dipentaerytrytol (DPE) and a non-organically-modified nanoclay (MMT) has also been observed in EVOH matrix: in facts DPE improves the intercalation of the MMT, promoting the penetration of the polymeric chains within the layers of the clays, and the MMT inhibits the DPE segregation for crystallization [18].

In order to obtain a wide overview of the structure and morphology of the polymeric composites, a methodology was applied, which uses the comparison of wide and small angle X-ray diffraction data and transmission electron microscopy as well.

The study by WAXD of polymeric nanocomposites is widespread, which is particularly interesting when the fillers are layered clays like MMT, which can give rise to intercalation and exfoliation, but less frequent is SAXS analysis, which is instead a technique of great impact because it allows defining in a careful manner, the interactions between polymer and clay, especially if coupled to the TEM. This approach is even more important in the nanocomposites studied in this paper where the synergistic effect of DPE and MMT is under investigation.

Furthermore, the comparison of WAXD data with those from thermal analysis allows obtaining detailed information on the crystallization processes induced by the presence of fillers and on any different crystalline phases that may be present in the prepared nanocomposites with respect to pure PA6.

Therefore, this paper aims at investigating the possibility of increasing PA6 performances by mixing some amounts of DPE and a non-modified nanoclay into the matrix. Then, the ultimate purpose of the current study is related to the strategies to extend the field of application of polymers by additives; this approach can prevent - to some extent - the use of much more expensive specialty polymers.

2. Experimental section

2.1. Materials

In the present work, the blends are based on PA6 (UBE Nylon 1022 B). Dipentaerythritol (DPE, Holtac™ D from Perstorp) and montmorillonite (MMT, Dellite HPS from Laviosa, deriving from a naturally occurring especially purified montmorillonite, not chemically modified) were used as additives.

2.2. Sample preparation

Before blending, all the materials were oven-dried overnight at 120 °C. The melt blending was carried out in a twin-screw extruder Coperion ZSK-18, characterized by a screw outer diameter of 18 mm. The 7 temperature modules were set as follows: $T_1 = T_2 = T_3 = T_4 = 260$ °C, $T_5 = T_6 = 270$ °C, $T_7 = 240$ °C. The feed rate was 2 kg/h and the screw speed 350 rpm; the pelletizer speed was set at 14 m/min.

Table 1
Composition and thermal data of PA6, DPE and the PA6-based binary blends.

Sample code		T_c[a] (°C)	ΔH_c[a] (J/g)	T_m[b] (°C)	ΔH_m[b] (J/g)
PA6[c]		188	69	222	82
DPE		200	270	224	273
	Composition PA6/DPE (wt/wt)				
PA_{95}/DPE_5	95/5	187	70	219	70
PA_{91}/DPE_9	91/9	180	65	217	89
PA_{77}/DPE_{23}	77/23	157 + 173	87	199 + 213	111
PA_{72}/DPE_{28}	72/28	162 + 171	100	200 + 209	114
PA_{67}/DPE_{33}	67/33	162	110	205	129
	Composition PA6/MMT (wt/wt)				
PA_{96}/MMT_4	96/4	182	58	221	56
PA_{93}/MMT_7	93/7	181	54	221	50
PA_{91}/MMT_9	91/9	180	52	221	47

[a] Measured during the cooling scan from the melt.
[b] Measured during the second heating scan.
[c] Extruded PA6 sample.

Binary blends obtained by varying the ratios between PA6 and DPE are listed in Table 1. The samples are indicated by the code PA_{XX}/DPE_{YY}, where XX and YY are the weight percentage of PA6 and DPE, respectively. Binary blends containing MMT are described in Table 1. Samples are called PA_{XX}/MMT_{ZZ}, where ZZ indicates the weight percentage of MMT. Ternary blends are described in Table 2 and are called $PA_{XX}/DPE_{YY}/MMT_{ZZ}$.

The blends, obtained by extrusion, were compression moulded into films by applying heat and pressure in a press (Alfredo Carrea, Genoa, Italy). The films were prepared by placing about 3.0 g of material between two metal plates positioned inside the press. The system was heated at 240 °C for 10 min and, after heating, the films were left inside the press until cooling to room temperature. Their thickness was about 0.3 mm.

2.3. Characterizations

2.3.1. NMR (Nuclear Magnetic Resonance) analyses

The ^1H NMR analysis was carried out using a Varian Mercury 400 MHz spectrometer; the samples were initially dissolved in non-deuterated 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and then diluted with deuterated chloroform in order to have a final mixture in 50/50 $CDCl_3$/HFIP volume ratio. The concentration of the resulted solution was 10 mg/ml with 0.03% (V/V) tetramethylsilane added as internal standard. The measurements were performed at 25 °C, accumulating 256 scans.

2.3.2. DSC (Differential Scanning Calorimetry) analyses

The calorimetric analysis was carried out by means of a Perkin-Elmer DSC6, calibrated with high purity standards (indium and phenantrene). The measurements were performed under nitrogen flow, using weighted samples (c.a. 10 mg) in aluminium pans. The thermal treatment consisted in a first heating scan to 260 °C and 1 min of isotherm to erase the thermal history; a cooling scan from 260 to 30 °C at 10 °C/min and 1 min of isotherm; finally, a second scan to 260 °C at