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Development of poly(vinyl chloride)/montmorillonite nanocomposites using chelating agents

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ABSTRACT

Different chelating agents such as poly(ethylene glycol), propylene glycol monooctadecanoate and palm oil were used for modification of the surface-treated montmorillonite (MMT). The work also included the development of a technique for mixing chelating agents with MMTs using different methods and different proportions of MMT/chelating agent/ethanol. Evaluation of the result of mixing was performed by thermogravimetric analysis, X-ray diffraction and high-resolution scanning electron microscopy (HR-SEM). The results showed that the chelating agents used were intercalated in MMT, increasing the interlayer spacing. The OMMT was used in the manufacture of composites with rigid PVC using a microcompounder. The master batch concept turned out to be promising in terms of dispersion and delamination of clay, as observed in HR-SEM photographs. However, despite good dispersion and exfoliation of MMT, poor compatibility between clay platelets and PVC matrix remains to be solved to enable full exploitation of its engineering potential. Despite this drawback, good thermal stability and mechanical properties have already been achieved.

1. Introduction

Polymer-layered inorganic nanocomposites have experienced an important development over the past 15 years. Substantial improvements in mechanical and physical properties brought about by polymer-layered silicate nanocomposites (PNC) have been frequently reported [1]. PNCs have the potential to exhibit significantly improved thermal, mechanical, optical and physicochemical properties compared with the bulk polymer or conventional composites. The degree of interaction between the polymer chains and the surface of the nanoparticles, the method of preparation of the sample, and the diameter of the nanofiller can drastically alter the chain segmental mobility and limit the number of conformations of the polymer, changing the properties of the system. The most commonly used layered silicate in PNCs is montmorillonite (MMT), an aluminosilicate smectite clay. This clay mineral is used because it is a cation-poor layered silicate, with layers that can be relative easily separated, or delaminated. More exactly, this clay has a low cation-exchange capacity (CEC) and, therefore, does not have a large number of ionic interactions holding the clay plates together [2]. Cation-rich clay species, such as vermiculite, are difficult to delaminate, and the ease of delamination becomes important in modification of the clay. MMT is also commonly used because it is environmentally friendly, readily available and its structure and chemistry have been well studied. However, the key factor to a successful result is exfoliation of the clay tactoids into individual layers and a good compatibility between silicate layers and the polymer matrix.

Because of the ionic nature, the galleries between the clay platelets are impervious to organic compounds. A common way of transforming the organophobic galleries is to exchange the galleries with alkyl ammonium cations, which have long organic chains with positively charged ends. These ends will attach to the negatively charged surface and make the galleries accessible to certain polymer molecules. It is important to note that the role of surface treatment is not only to provide the clay with an organophilic surface, improving the wetting characteristic with the polymer, but to increase the interlayer distance as well [3]. However, the choice of the optimal modifier is currently at best empirical. Researchers currently focus most efforts on developing interfacial tailoring that achieves dispersion, without regard to providing the necessary thermal stability and desired interfacial response for final form processing or a predetermination of the desired interfacial characteristics (e.g., strong, intermediate or weak bonding) to maximize material performance. However, these latter considerations are paramount to providing components that have a reliable service life.

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Despite the fact that poly(vinyl chloride) (PVC) is one of the major thermoplastic polymers, having been widely used in industrial fields for many years, PVC/MMT nanocomposites are still in the introductory phase. PVC itself has a number of advantageous properties, such as nonflammability, low cost and formulating versatility, but is also subject to some limitations because of its inherent disadvantages, such as low thermal stability, brittleness and low softening temperature. In recent years, the prospect of developing PVC nanocomposites with significantly improved properties has attracted increasing attention. PVC/cellulose whiskers [4], PVC/nano-$CaCO_3$ [5] and PVC/MMT [6–8] have been studied. One of the major problems in preparation of PVC/MMT nanocomposites is organic surface modification of MMT (OMMT). There are two main methods that can be used to make the clay organophilic, viz., ion-exchange and ion-dipole methods.

Most of the efforts have been performed with the ion-exchange method using quaternary ammonium salts; however, PVC is visibly discoloured and degraded during melt blending with such OMMT, because the quaternary ammonium salts decompose into tertiary amines, which normally catalyse the dehydrochlorination of PVC [9,10].

This work is based on the idea of using suitable chelating agents as organic modifiers that are capable of decreasing the electrostatic forces between the negatively charged flakes of MMT and the positive ions in the interlayer spacing.

2. Experimental

2.1. Materials

The materials used in this study are summarized in Table 1. Suspension PVC compounds were provided by Ineos ChlorVinyls, Norway and contained a standard additive package including a calcium/zinc stabilizer.

Table 1
The list of components.

Component	Designation	Supplier
PVC rigid grade	Norvinyl S5745	Hydro Polymers AB
PVC rigid grade	Norvinyl S6045	Hydro Polymers AB
MMT-PV	$A_f = 150–200$	Nanocor Inc.
MMT PN	$A_f = 300–500$	Nanocor Inc.
Commercial OMMT	NANNOLIN DK3	Zhejiang Fenghong Clay Chemicals Co.
Propylene glycol monostearate	Kessco PEG MS (C16: 47–53%, C18: 41–51%)	Akzo Nobel
Polyethylene glycol	Witconol PEG-400	Akzo Nobel
Palm oil[a]	Material no. 026754	Danisco Emulsifiers

[a] Concentration of fatty acids in palm oil:
Saturated (total: 49.9%): Palmitic C16:0 45%, Stearic C18:0 4.5%.
Monounsaturated: Oleic C18:1 38%.
Polyunsaturated: Linoleic C18:2 10%.

2.2. Preparation of OMMT

The silicate layers in MMT have a slightly negative charge that is balanced by exchangeable ions in the gallery spaces (in the natural form of MMT, predominantly Ca^{2+}, Mg^{2+} or Na^{+} ions). The interlayer cations also hold the clay layers tightly together because they can be shared by two neighbouring platelets. The electrostatic forces that hold stacks of clay platelets together make it difficult to disperse individual platelets throughout the polymer matrix. However, there are certain organic compounds that are capable of forming coordinate bonds with metals through two or more atoms of the organic compound; such organic compounds are called chelating agents. Our idea was to use chelating agents that are specific for the cations in MMT. In this way, the charge can be partly screened off and the chelating agent can increase the interlayer spacing, particularly if it is a bulky molecule. In principle, chelating has been used in many other instances, e.g., polyols to decrease the catalytic effect of $ZnCl_2$ in Ca–Zn-stabilized PVC. Three different chelating agents were used in this investigation, viz., propylene glycol monostearate (PEG MS), polyethylene glycol (PEG 400) and palm oil.

To modify MMT, chelating agents were added to water or ethanol and mixed using a Janke & Kunkel Ultra-Turrax high-speed mixer. Then a predetermined amount of MMT was added followed by vigorous mixing. During mixing, friction caused an increase in temperature to 75 °C. The resulting slurry was filtered to remove superfluous solvent. Finally, the filter-cake was dried in a vacuum at 50 °C to obtain modified clay consisting of MMT and organic modifier only. Theoretically, 30:9 parts of MMT:modifier is the rough stoichiometric ratio required to screen all interlayer cations. The 30:18 and 30:30 ratios were also used, which gave a surplus of modifier.

2.3. Processing

The method of direct melt intercalation has become a mainstay for preparation of PNCs because of its convenience for industrial uses. The melt compounding is effective whenever the thermodynamics of the melted polymer/organoclay mixture allows the polymer chains to penetrate into the clay interlayer spaces and thus push the individual layers apart from each other. When the melt intercalation approach is used, it is commonly advantageous to use a "master batch" production [11].

Because of the large number of formulations that it was necessary to prepare, it became important to use an efficient and rapid manufacturing process. Therefore, the crucial tool was a 15 cm^3 laboratory-scale twin-screw extruder Xplore 15 microcompounder equipped with a 5.5 cm^3 shot volume injection moulder. The high throughput (HT) nature of the microcompounder was derived from three important abilities, namely, to alter the formulation quickly, to change the processing conditions easily and to perform direct extrusion of the test samples suitable for the evaluation.

At the beginning of this investigation, a one-step melt process was applied. However, drawbacks of this method were soon discovered and henceforth all samples were extruded in the microcompounder using a two-step melt process. In the first step a master batch (MB) was produced with a content of 20 phr (parts per hundred parts PVC) MMT. In the second step, the MB was mixed with stabilized PVC to achieve the final composition. Different set points were tried for each material, aiming to find an optimum in terms of temperature, shear and residence time. Specimens for mechanical testing were moulded using a DSM Research 10 ml injection-moulding machine. Before extrusion, all ingredients were mechanically mixed together at 90–100 °C for 15 min using a rotary stirrer.

2.4. Thermogravimetric analysis (TGA)

A high-resolution thermogravimetric analyser (TA type TGA 2950) was used to determine the percentage of organic modifier in various OMMTs and the decomposition temperature. High-resolution TGA is normally used when improved separation within a shorter time is required. The MMT-containing samples were analysed under a flowing nitrogen atmosphere. The temperature scans ranged from 30 to 900 °C.