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Influence of the intercalated cations on the surface energy of montmorillonites: Consequences for the morphology and gas barrier properties of polyethylene/montmorillonites nanocomposites

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Abstract

Organically modified montmorillonites obtained by cation exchange from the same natural layered silicate were studied. The surface properties of the pristine and a series of organically modified clays were determined by inverse gas chromatography and the water adsorption mechanisms were studied by a gravimetric technique coupled with a microcalorimeter. A significant increase of the specific surface area, a decrease of the water adsorption, and a decrease of the dispersive component of the surface energy were observed when the sodium cations of the natural montmorillonite were exchanged for a quaternary ammonium. Slighter differences in surface properties were observed, on the other hand, between the different types of organically modified montmorillonites. Indeed, similar dispersive components of the surface energy were determined on the organoclays. Nevertheless, the specific surface area increased in the range 48–80 m^2/g with increasing d-spacing values and the presence of specific groups attached to the quaternary ammonium, such as phenyl rings or hydroxyl groups, led to some specific behaviors, i.e., a more pronounced base character and a higher water adsorption at high activity, respectively. Differences in interlayer cation chain organization, denoted as crystallinity, were also observed as a function of the nature of the chains borne by the quaternary ammonium. In a later step, polyethylene-based nanocomposites were prepared with those organically modified montmorillonites. The clay dispersion and the barrier properties of the nanocomposites were discussed as a function of the montmorillonite characteristics and of the matrix/montmorillonite interactions expected from surface energy characterization.

Keywords: Montmorillonites; Water adsorption; Surface energy; Nanocomposites; Gas permeability; Morphology

1. Introduction

Interfacial interactions play an important role in the control of the properties of multiphase systems and particularly of particulate-filled polymers. These interactions become essential for the dispersion of nanofillers in a polymer matrix and they are also at the origin of the formation of an interphase that can have a determining effect on the mechanical properties but also on specific properties such as barrier properties [1–5]. Lamellar nanofillers such as montmorillonite are often dispersed in polymer matrices to increase the gas barrier properties from a tortuosity effect [6–10]. These fillers are clay minerals 2:1 phyllosilicates: two Si tetrahedral sheets are separated by one Al octahedral sheet (T–O–T). The isomorphic substitutions in the sheets originate deficits of positive electric charges. These charges are balanced by exchangeable cations such as Na^+ in interlayer positions.

When poor polymer/particle interactions are developed in the composite systems, the dispersion of individual platelets is not achieved and a weak interface can even be created. This interface can have some consequences for the barrier properties. Particularly, it can lead to an increase of the permeability over the original polymer because of bypass of gas penetrants

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around the particles [11]. Thus it is important to create particle/matrix interactions strong enough to get platelets highly dispersed within the polymer matrix and strong interactions at the interface.

Organically modified montmorillonites have been developed, then, by intercalating organic species within the interlayer sites of the natural montmorillonites [12–17] in order to promote the interactions that favor the insertion and diffusion of the polymer chains in the interplatelet galleries. Quaternary ammoniums bearing long alkyl chains have been particularly used with polyolefin matrices, whereas quaternary ammonium bearing hydroxyl groups have been preferentially used with more polar matrices such as polyamides. If a lot of studies [8–17] have been concerned with the final properties of these different organoclay/polymer nanocomposites and have shown that it was easier to obtain exfoliated structures and enhanced gas barrier properties with polar matrices than with apolar matrices, despite the clay modification and the use of a compatibilizer, very few studies have dealt with the characterization of the clays as a function of the interlayer cation [18–26], particularly to understand the clay/polymer interactions.

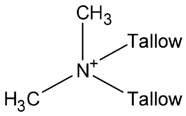
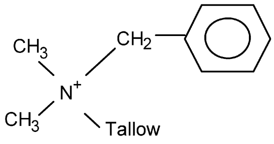
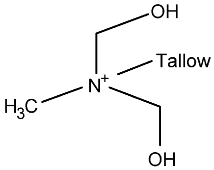
The present work has focused on the detailed study of organically modified montmorillonites obtained by cation exchange from the same natural montmorillonite. Particular attention has been paid to the cation chains' organization and mobility in the interplatelet gallery, to the clay interaction capacity for probe molecules making it possible to determine the surface tension of the fillers, and to the accessibility of specific functions beared by the cations. The morphology and gas barrier properties of polyethylene-based nanocomposites have then been discussed as a function of the montmorillonites characteristics. These ones are indeed important for the understanding of clay/polymer chain interactions and they are determining parameters for the final nanocomposite properties.

2. Experimental

2.1. Materials

The montmorillonites considered in this study, a natural sodium montmorillonite (Nanofil 757) and three organically modified montmorillonites (Nanofil 15, Nanofil 919, and Nanofil 804), were commercial montmorillonites provided by Süd Chemie. The exchange capacity of the natural layered silicate was equal to 100 mequiv/g and all the organically modified montmorillonites studied in this work were obtained by cation exchange from this natural montmorillonite. The quaternary ammoniums used for the exchange reactions are presented in Table 1 and the following abbreviations were used to design the different montmorillonites: MMT–Na for the natural montmorillonite, MMT–DMDT for the montmorillonite bearing a dimethyl ditallow quaternary ammonium as cation, MMT–DMBT for the montmorillonite bearing a dimethyl (benzylmethyl) tallow quaternary ammonium, and MMT–DHMT for the montmorillonite bearing a di(hydroxymethyl) methyl tallow quaternary ammonium.

Table 1
Montmorillonites used in the study

Commercial name	Abbreviation	Cation	Organic content[a] (%)	d_{001}[b] (Å)
Nanofil 757	MMT–Na	Na^+	–	
Nanofil 15	MMT–DMDT	 Tallow: 65% C18–30% C16–5% C14	35.7	28
Nanofil 919	MMT–DMBT		33.75	18.8
Nanofil 804	MMT–DHMT		30.08	18

[a] Organic content of the different MMTs determined by TGA.

[b] Interplatelet distance determined by XRD at room temperature.

The polyethylene used in this study, named HDPE, was a high-density polyethylene (Eraclene ML 74 from Polimeri Europa) having a molar mass of 122,400 g/mol. A maleic-anhydride-grafted high-density polyethylene (Priex 12030 from Solvay), denoted HDPE–g-MA, with a molar mass equal to 61,600 g/mol was used as interfacial agent.

2.2. Methods

2.2.1. Montmorillonites characterization

Thermogravimetric analysis experiments were performed with a TGA apparatus (TGA 2950-TA Instruments) from 30 to 550 °C at 10 K/min under helium. The mass loss with increasing temperature, as well as its first derivative, which represents the change in degradation rate, were plotted. The nanofiller organic content was also determined.

Differential scanning calorimetry data were measured on 10-mg montmorillonite samples under helium using a DSC 2920 apparatus from TA Instruments. Two scans from −40 to 150 °C at a heating rate of 10 K/min were successively recorded with an intermediate cooling at 10 K/min.

Wide-angle X-ray diffraction experiments, XRD, were performed between 1° and 10° by steps of 0.02° using a Siemens D500 diffractometer to get d-spacing, d_{001}, that corresponds to the distance between the top of the Si tetrahedral silica sheet (T) and the top of the Si tetrahedral sheet in the next layer. The experiments were made on the montmorillonites conditioned under atmospheric pressure at room temperature.

The surface tension of the nanofillers was determined by inverse gas chromatography (IGC) at infinite dilution using an apparatus from Agilent Technologies equipped with a flame ionization detector. N-alkanes with different chain lengths were