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Structure and surface coverage of water-based stearate coatings on calcium carbonate nanoparticles

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ABSTRACT

In a preceding paper it was found that, during coating with solutions of a stearin salt in water, whatever the concentration used, a considerable part of the PCC surface remains free, indicating the development of an incomplete monolayer. This was explained by assuming a micelle adsorption mechanism as the dominating process in water, resulting in the formation of a multilayer structure composed of an inner incomplete chemisorbed monolayer and one or more physically adsorbed layers. This model predicted a physisorbed layer in which polar groups are oriented outwards of the particles, resulting in a hydrophilic surface, and contrary to experimental evidence. In this paper we propose that during the drying stage the physisorbed calcium stearate layers undergo a complex rearrangement leading to a hydrophobic coating with the aliphatic tails oriented outwards of the particles. The results of XRD measurements proved that the physisorbed stearate layer is crystalline, while DSC model experiments indicated that the layer goes through phase transitions during heat treatment. The proposed model matched with IGC measurements, showing a clear dependence of the specific component of surface energy on the amount of absorbed stearin. The agreement with values obtained for solvent and dry-coated particles support the proposed rearrangement of alkanoate molecules in the coating.

1. Introduction

The aim of the surface coating of precipitated calcium carbonate (PCC) nanoparticles is to achieve good dispersion in a polymer matrix that is necessary to obtain good composite properties including toughness [1–4]. The most widely used surfactants are fatty acids and industrial coating is done in water because of the low cost and simplicity of the process [5,6]. However, previous studies on the surface characterization of PCCs coated with stearic acid have been carried out almost exclusively in either dry conditions using a high speed mixer (dry-blending or dry-coating), or in the solution of a good solvent of stearic acid (e.g. toluene). For example, Osman and Suter [7] found that solvent coating of calcium carbonate with stearic acid resulted in the formation of a monolayer of chemisorbed calcium bicarbonate due to the reaction of one stearic acid molecule with one calcium cation. The addition of surplus stearic acid led to the formation of free stearic acid physically adsorbed onto calcium carbonate particles. The physisorbed coating could be easily removed by a good solvent of the acid. Similar results were reported in the literature for dry-coating [8,9]. Li and co-workers [10] studied the behavior of $CaCO_3$ nanoparticles with controlled coverage, which were prepared in solution of water and alcohol in a volume ratio of 3:1. According to two recent reviews by Rothon [11,12], the mechanism of coating for calcium carbonate particles from aqueous solution has not been reported in any detail.

Other papers discussed the effect of the amount of surface coating on the final properties of polymer nanocomposites. The optimum level of surface coating was found to correspond to the minimum of surface tension [13–15], which is reached at complete monolayer coverage, or rather, when all active sites on the surface of calcium carbonate react with stearic acid molecules. Surface coating of PCC with stearic acid considerably reduces its surface tension from about 210 to 40–60 mJ/m^2 [16]. Some researchers encountered problems during the processing of HDPE based composites filled with dry-coated PCC particles with stearic acid content in excess of the amount required to reach a full monolayer. Moreover inferior tensile strength, together with larger Young's modulus were reported for materials filled with PCC particles dry-coated with excess stearic acid, compared to composites filled with the same filler coated with the amount necessary to reach monolayer coverage [17].

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Limited information is available about the adsorption of stearic acid onto the surface of PCC in aqueous medium. While the mechanism of surface coating has been recently elucidated [18], the structure obtained in such a process is not completely clear, although this is the usual method in the industry for the coating of such fillers. A previous study carried out by our group yielded interesting results about the water coating process of PCC nanofillers, the mechanism of which differs from that occurring in dry or solution coating [18]. We could show that alkanoate molecules[1] form two types of coating layers with different physico-chemical characteristics: a chemisorbed monolayer with the acid groups in the carboxylated form interacting with basic surface sites, i.e. the coating is in the form of a partial or half salt, >Ca COOR, where R represent the aliphatic tail and the symbol > the surface site, and one or more physisorbed calcium alkanoate (mainly calcium stearate, $CaSt_2$, and calcium palmitate $CaPm_2$) layers. These fatty acid salts are not associated with the filler surface and are only weakly attached to the surface monolayer. More interestingly, the consideration of the surface covered by a single stearate molecule, defined by its cross-sectional area, the specific surface area of the particles, and the orientation of the surfactant molecules revealed that the surface of PCC is covered only partially with the chemisorbed monolayer, while a significant part of it remains free. This experimental observation was tentatively explained by a micelle adsorption mechanism that results in an inner incomplete chemisorbed layer and one or more physically adsorbed layers. The logical consequence of this model is that the polar carboxyl groups in these outer layers should be pointing away from the surface of the particles. This should result in a hydrophilic surface and large surface energy for these particles in contradiction with the experimental evidence of a better dispersion of coated nanoparticles in polyolefins during melt blending [1].

The main purpose of this work is to resolve this contradiction and improve the picture presented in our previous paper. Thus the structure of surface coating is further investigated, particularly in relation to the phase transitions taking place in the physisorbed calcium alkanoate layers, weakly linked to the incomplete chemisorbed layer, during the drying stage [18]. In fact, those physically adsorbed layers play a critical role in the dispersion of the particles in the polymer during melt blending, and act as an interface or interphase when precipitated calcium carbonate is applied as a filler in particulate-filled polymers [1,19]. Thus a proper control on the structure and composition of these layers is very relevant in order to tailor the final mechanical properties of the composites.

Calcium stearate and calcium palmitate forming the physisorbed multilayer are typical soaps (salts of fatty acids) of amphiphilic nature consisting of a long hydrocarbon (or paraffinic) chain attached to a polar carboxyl group. Each molecule thus consists of two parts with clearly differing physical and chemical properties: the paraffinic chains are hydrophobic and interact through Van der Waals forces, while the carboxyl groups are essentially soluble in water and associate by dipole interactions. The interaction of the long aliphatic chains results in their crystallization, and depending on thermal conditions the molecules arrange in different ways and exist in different crystalline forms.

The thermal behavior and the polymorphism of crystalline calcium stearate have been well documented in detail by Vold et al. [20,21], Lelann and Bérar [22] and Garnier et al. [23] using experimental techniques such as X-ray diffraction, thermogravimetry and scanning calorimetry. They showed that the structure prevailing at room temperature is extremely sensitive to the presence of impurities, like water or glycerol, and to thermal treatment. Also the method of manufacture, especially the maximum processing temperature and aging can affect the final structure obtained. From room temperature to about 123 °C, the chains and carboxyl groups are perfectly stiff and fully crystallized, although two distinct lamellar crystalline phases may form[2]: one stable up to 104 °C, and the other between 104 °C and 123 °C, termed C1 and C2, respectively [23]. In the C1 phase range, below 104 °C, calcium stearate may exist in a monohydrate monoclinic α phase (corresponding to the stacking of four molecular layers), and two anhydrous forms: orthorhombic β and the γ (undetermined structure) phase [22,23]. Several thermotropic phase transitions were observed within these phases. Dehydration of the α form leads to a mixture of β and γ modifications, the relative amount of which depends on dehydration temperature and probably on heterogeneities. In the C2 phase the molecules of calcium stearate are arranged into a hexagonal lattice, a less ordered structure in which the paraffin chains attain a certain freedom of rotation about their main axis [24]. At 104 °C, both the monohydrate α and the anhydrous β phases transform into the C2 phase [23]. On cooling back to room temperature, the C2 form is stable down to 65 °C, when the orthorhombic β' phase (a poorly crystallized β phase) appears, whatever was the initial state, either α or β. Above 120 °C, further mesomorphic, liquid crystalline phases form with the corresponding transitions at 124, around 150 and 195 °C [20,23]. It is obvious that the actual structure of calcium stearate depends on its preparation conditions, thermal history and the extent of dehydration.

The goal of the present study was to obtain more information about the water coating of PCC nanoparticles with fatty acids with particular interest to surface coverage and to the structure of the coating formed. Both are important in practice since they determine the level of dispersion achieved during the melt blending or industrially relevant polymers. DSC measurements were used for the determination of the degree of surface coverage in the chemisorbed layer. The thickness of the coating was estimated from XPS measurements using island-on-sphere model calculations. Additionally, the surface energy of PCC particles was also determined by IGC in this study in order to obtain further information about the orientation of the stearate molecules and to predict the strength of interfacial interactions in polymer composites.

2. Experimental

2.1. Materials

A series of experimental precipitated calcium carbonate (PCC) samples were supplied by Solvay Advanced Functional Minerals (Salin-de-Giraud, France). The samples were surface treated in aqueous solution with a commercial stearin, Pristerene 4937, supplied by Uniqema (now Croda Italiana S.p.A., Mortara, Italy) in the nominal concentration range of 0–13.5 wt.%. These fillers were coded from PCC1 to PCC9 corresponding to increasing coating levels. The size of the particles was about 62 nm with the corresponding specific surface area of 19 m^2/g as shown in Table 1. PCC3 is reported with a coating amount of 6.6 wt.%, which is larger than expected maybe due to the imperfect control of the surface coating process. Considering the choice of the surfactant used in this work, we must call the attention to the fact that industrial calcium carbonates are coated with commercial stearin and not with pure stearic acid. The commercial stearin chosen, Pristerene 4937, is a blend of mainly stearic acid (octadecanoic acid, C18:0, molar mass 284.5 g/mol), palmitic acid (hexadecanoic acid, C16:0, molar mass

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[1] Commercial stearic acid, known as stearin, is in fact a blend of mainly stearic and palmitic acids. Here and in the following text we refer, for simplicity, to the calcium salt of stearin sometimes as "stearin soap" or, in other cases, "stearin alkanoate". The two terms are used as synonyms. When there is the possibility of a misunderstanding we also refer to stearate/palmitate salts for the salts of stearin, and pure calcium stearate as the calcium salt of pure stearic acid.

[2] The lamellar phases are formed by stacked bilayers (one dimensional ordering).