Research paper

Influence of Hansen solubility parameters on exfoliation of organophilic fluoromica

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ABSTRACT

The influence of different surface energies described by Hansen solubility parameters (HSP) on the exfoliation of organophilic fluoromicas is investigated. HSP values of four synthetic organophilic fluoromica with different surfactants have been predetermined. Those surfactants change the fluoromica surface energies described by HSP. The HSP are used to calculate the dispersibility of the various organophilic fluoromica in chloroform via Flory-Huggins (F-H) theory. The F-H parameter (χ) describes the effective difference in HSP related surface energies of particles and chloroform molecules, which is related to the energy cost of exfoliation. An influence of F-H parameter is detected on the delamination state of organophilic fluoromica. The delamination state is evaluated quantitatively using atomic force microscopy (AFM). In the case of a high F-H parameter ($\chi > 0.15$), aggregated and unstable fluoromica dispersions are obtained. Whereas in the case of F-H parameters near zero, exfoliated and stable fluoromica dispersions are achieved. The presence of surfactant on the surface of exfoliated fluoromica flakes is proven by Fourier-transform infrared spectroscopy (FT-IR), and density functional theory (DFT) calculation.

1. Introduction

In recent years, clay/polymer nanocomposites (CPN) have generated great interest both in industry and academia, as these often exhibit remarkable improvement in material properties. Organic material properties such as high mechanical flexibility and transparency can be reinforced (Utracki et al., 2007), or protected against gases (Lape et al., 2004) by combining them with inorganic fillers. The most frequently used clay minerals in nanocomposites belongs to a family of 2:1 phyllosilicates, which have a sheet silicate structure, such as montmorillonite, hectorite, and vermiculite (Ray and Okamoto, 2003).

A particularly interesting type of synthetically prepared clay is synthetic fluoromica. Such fluoromica is synthesized by introducing an alkali metal in talc interlayer galleries, which is achieved by heating talc with an alkali fluorosilicate for several hours (Souza et al., 2011). The method for producing semi-synthetic fluoromica (Somasif) was patented by Tateyama et al. (1993). According to this patent, a powdered mixture of 10 to 35 wt% alkali silicofluoride (Na_2SiF_6 with optionally LiF) and natural talc is heated for about one hour at a temperature of around 700 to 900 °C. The product has the composition: $\alpha MF \cdot \beta (aMgF_2 \cdot bMgO) \cdot \gamma SiO_2$ where M is an alkali metal such as sodium or potassium, and α, β, γ, a, b are coefficient satisfying the

relationships of $0.1 \leq \alpha \leq 2$; $2 \leq \beta \leq 3$; $3 \leq \gamma \leq 4$; and $a + b = 1$ (Tateyama et al., 1993).

The Somasif minerals are expandable phyllosilicate with high lateral sizes (up to 6000 nm), structures similar to montmorillonite (MMT) and a cation exchange capacity (CEC) of $1.2 \frac{meq}{g}$ (Utracki et al., 2007). They have a hydrophilic character but can be intercalated with quaternary ammonium ions to obtain organophilic fluoromica (OM).

In nanocomposites, the morphology of clay varies between: aggregated, partially delaminated (intercalated) and complete delaminated (exfoliated) (Tan and Thomas, 2016). When the exfoliated state is reached, each particle is completely broken down to single layered platelets. Such a structure is the most desirable, as it can provide excellent thermal and mechanical properties at very low clay content (Ray and Okamoto, 2003). However, in reality, most nanocomposites are in an intermediate state between aggregation, intercalation or exfoliation. For the exfoliation of clay, challenges arise from the targeted high surface area and the electrostatic forces between the layers. Clay layers cannot be separated by simply introducing mechanical force using an ultrasonicator or a high shear disperser due to strong electrostatic forces between layers. Intercalation of surfactants into clay interlayer space is commonly used to reduce such electrostatic forces. As a result of this intercalation, the interlayer space increases. Higher distances

weaken attraction forces and lower the energy barrier needed to exfoliate the material in a solvent or monomer (Nicolosi et al., 2013). However, the modification of the clay alone is not enough to promote delamination processes in solvents or polymers (Hojiyev et al., 2017). The understanding of delamination processes of organophilic clay in organic solvents or polymers is critical to prepare nanocomposites with exfoliated clay.

For the investigation of such clay delamination processes, a number of research groups have used surface energy (Choudhury et al., 2009; Hojiyev et al., 2017; Vaia and Giannelis, 1997; van Oss and Giese, 1995, 2003) and solution parameters (Choudhury et al., 2009; Ho et al., 2001; Ho and Glinka, 2003; Hojiyev et al., 2017; Jang et al., 2005; Krikorian and Pochan, 2003; Lu et al., 2004; Petersen et al., 2015; Yousfi et al., 2013).

For the solubility parameter approach, group-contribution methods are often used to calculate Hildebrand (Choudhury et al., 2009; Ho et al., 2001; Ho and Glinka, 2003; Jang et al., 2005; Krikorian and Pochan, 2003; Petersen et al., 2015; Yousfi et al., 2013) or Hansen solubility parameters (HSP) of the modified clay (Hojiyev et al., 2017; Lu et al., 2004). Those estimations are based on the structure of surfactant and require certain assumptions. Main assumptions of group-contribution methods are to use CN or N group instead of quaternary ammonium ions (Choudhury et al., 2009; Hojiyev et al., 2017; Petersen et al., 2015; Yousfi et al., 2013) or that only the longest aliphatic chain groups of surfactants contribute and that the quaternary ammonium group is neglected (Ho and Glinka, 2003; Hojiyev et al., 2017; Jang et al., 2005; Krikorian and Pochan, 2003). The influence of clay on the solubility parameters cannot be calculated by using the group-contribution method. A few Hildebrand parameters were evaluated based on real data. One approach by monitoring the change of organic layer thickness of intercalated surfactants in different solvents via small-angle neutron scattering (SANS) (Ho et al., 2001) or by calculate the Hildebrand parameters based on surface tension data (Beerbower, 1971).

Hernandez and Coleman with coauthors have shown a method to measure Hansen solubility parameters (HSP) of graphene (Hernandez et al., 2010), molybdenum disulfide, tungsten disulfide or boron nitride (Coleman et al., 2011). For that, they stressed dispersions and afterward estimated the concentration of filler in solvents by measuring their optical absorbance. The measurements have shown that exfoliated flakes can be obtained in dispersions with similar HSP. In previous work, a method to measure HSP for organophilic fluoromica was developed. In contrast to the Coleman approach, the parameters were obtained using gravimetric analysis due to the absence of absorbance bands in the UV–Vis spectra (Huth et al., 2018).

In this study, the influence of different surface energies described by Hansen solubility parameters (HSP) on an exfoliation process of different organophilic Somasif in chloroform is investigated. For that four different organophilic micas (OM) are used for this evaluation, one self-prepared and three commercially available Somasif. Predetermined HSP allows calculating the dispersibility of each Somasif in chloroform via Flory-Huggins (F-H) theory. F-H parameter describes the effective difference in HSP related surface energies of particles and chloroform molecules, which is related to the energy cost of exfoliation (Hernandez et al., 2010). The influence of F-H parameter on the dispersibility of Somasif in chloroform is investigated. The delamination state is evaluated quantitatively using atomic force microscopy (AFM). The presence of surfactant on the surface of exfoliated fluoromica is proven by Fourier-transform infrared spectroscopy (FT-IR), and density functional theory (DFT) calculation.

2. Experiment

2.1. Chemicals

CBC. Co supplies synthetic fluoromicas, namely Somasif™. Non-modified Somasif (ME-100), as well as three organophilic synthetic fluoromica, are used: Somasif MEE, MTE, and MAE. Chloroform, as well

as the surfactants Arquad 2HT-75 (2HT-75), are supplied by Sigma-Aldrich. All materials mentioned above are used as received without further purification.

2.2. Organic modification of Somasif

The modification of ME-100 with 2HT-75 was done according to previews work (Huth et al., 2018).

2.3. Delamination process

In a 10-ml flask, Somasif was dispersed into chloroform via an Ultra-Turrax® dispersion instrument. In all experiments 15 $\frac{mg}{ml}$ was used as initial concentration. The samples were dispersed in chloroform at a predetermined speed and time (12k rpm for 5 min). After the dispersion step, samples were centrifuged at 2k rpm for 5 min. The supernatant was collected for further analysis. Somasif dispersions were drop-casted on a Si wafer with a 100 μm SiO_2 layer. Chloroform was evaporated by heating up the sample. The remaining flakes were analyzed to understand the morphology and delamination status.

2.4. Characterization

The dispersibility of the organophilic fluoromica (Somasif) was characterized as the concentration of the mineral in the supernatant. Volumes of 1 ml of those dispersions were filled into Eppendorf tubes. Chloroform was then slowly evaporated under vacuum. The solid content was weighed with a microscale and the concentration/dispersibility of Somasif in the dispersion was calculated. The delamination state of casted Somasif was investigated using atomic force microscopy (AFM) measurements. For those measurements, a Nanosurf Mobile S was used. FT-IR was performed with a Nicolet-Avatar 370 instrument in transmission mode. Scanning was performed in a range of 400–4,000 cm^{-1}. All samples were analyzed in form of potassium bromide (KBr) tablets. Furthermore, the transmission spectrum of surfactant molecules without anion, was calculated by density functional theory (DFT) via Gaussian 09 using basis set 6-31G, functional B3LYP and a frequency scaling of 0.962 (Becke, 1993; Frisch et al., 2009; Kohn and Sham, 1965; Lee et al., 1988).

3. Results and discussion

3.1. Influence of Hansen solubility parameters and Flory-Huggins parameter on dispersibility

Hansen solubility parameters (HSP) are useful when it comes to select solvents for a given liquid or polymer. The basis of those parameters is the distinction of the total energy of vaporization of a liquid in several individual parts. These arise from (atomic) dispersion forces E_D, (molecular) permanent dipole-permanent dipole forces E_P, and (molecular) hydrogen bonding forces (electron exchange energy) E_H (Hansen, 2007).

$$E = E_D + E_P + E_H \tag{1}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{2}$$

δ_D, δ_P, and δ_H are the Hansen solubility parameters for the dispersion, polar and hydrogen bonding (H−bonding) interactions [$\sqrt{MPa}$].

Hernandez and Coleman with coauthors have shown exfoliated and stable dispersions of graphene, molybdenum disulfide, tungsten disulfide, boron nitride, which were obtained in solutions with well-defined HSP (Coleman et al., 2011; Hernandez et al., 2010). In a previous work, the HSP of the used organophilic fluoromica (Somasif) were obtained using a modified Coleman approach via gravimetric analysis (Huth et al., 2018). Table 1 shows the surfactant structures and organic content of the used Somasif (MEE, MTE, MAE and S-2HT-75), which are different quaternary ammonium ions.