Research paper

Measurement of Hansen solubility parameters for organophilic fluoromica and evaluation of potential solvents for exfoliation

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ABSTRACT

A method to measure Hansen solubility parameters for organophilic fluoromica is developed. For this purpose, fluoromica with four different intercalated molecules (surfactants) have been dispersed in various solvents. These surfactants change the fluoromica surface energies described by Hansen solubility parameters (HSP). The three Hansen solubility parameters (dispersion, polar and hydrogen bonding) of different organophilic fluoromicas have been obtained by using gravimetric analysis. The dispersion parameters for all four organophilic fluoromicas are almost identical, with a value around $17 \sqrt{MPa}$. Whereas polar and H-bonding parameters are varying with the used surfactants. Surprisingly the polar and hydrogen bonding values for hydrophobic alkyl chain tailored surfactants are higher than those for a hydrophilic surfactant with poly(ethylene glycol) chains. The determined HSP values allow calculating the dispersibility of the organophilic fluoromica in solvents via the Flory-Huggins (F-H) parameter. These F-H parameters describes the effective difference in HSP related surface energies of particles and solvent molecules and are used to identify potential solvents for an exfoliation process. With this approach, beside known solvents such as chloroform, also new potential candidates such as trichloroethylene, and benzyl ethyl ether are identified for dispersing/exfoliating modified organophilic fluoromica. This work is accompanied by X-ray diffraction (XRD) measurements to gain knowledge about the interlayer space of the different organophilic fluoromicas.

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 protection 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 consist of a sheet silicate structure, such as montmorillonite, hectorite, and vermiculite (Ray and Okamoto, 2003).

A particularly interesting type of synthetically prepared clay is synthetic Somasif mica. Such mica, are synthesized by introducing an alkali metal in talc interlayer spaces, which is achieved by heating talc with an alkali fluorosilicate for several hours (Souza et al., 2011). Somasif mica is obtained when Na_2SiF_6 is used. Tateyama et al. (1993) patented the method for producing semi-synthetic Somasif fluoromica.

The Somasif mica minerals are expandable phyllosilicates with high lateral sizes (up to 6000 nm) and structures similar to montmorillonites (Utracki et al., 2007). They have a hydrophilic character, but can be intercalated with quaternary ammonium ions to obtain organophilic mica (OM).

In nanocomposites, three types of morphologies are found based on the degree of clay delamination: aggregated, partially delaminated (intercalated) and complete delaminated (exfoliated) (Tan and Thomas, 2016). In the exfoliated state, each particle is completely broken down to single layered platelets. The exfoliated structure is the most desirable state, as it can provide excellent thermal and mechanical properties at very low clay content (Ray and Okamoto, 2003). However, 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 held together by strong electrostatic forces cannot be separated by simply introducing mechanical force using an ultrasonicator or a high shear disperser. To reduce such electrostatic forces, intercalation with surfactants is commonly used in industry. These surfactants intercalate into the interlayer space. As a result, the interlayer space increases. This weakens attractive forces and lowers the

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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, as well as the stability of such dispersions, is a critical step towards preparing exfoliated clay in nanocomposites.

To this end, 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 investigation of such delamination processes on clay.

In the case of surface energy approach, contact angle measurement of clay with solvents of known surface energy, along with the Young-Dupre equation is used to evaluate surface tension (van Oss and Giese, 1995). Comparing the surface tension of clay, solvent, and polymer can give a way to predict clay-solvent or clay-polymer interactions. Unfortunately, these surface energies are known for just a small number of solvents or polymers. A comprehensive comparison with experimental data is difficult due to the limited availability of those measured values (Vaia and Giannelis, 1997).

In the case of 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 calculations are based on the structure of surfactant and require certain assumptions. Main assumptions of those calculations are 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) or to use CN or N group instead of quaternary ammonium (Choudhury et al., 2009; Hojiyev et al., 2017; Petersen et al., 2015; Yousfi et al., 2013). The influence of clay minerals on the solubility parameters cannot be calculated by using the group-contribution method. A few Hildebrand parameters were evaluated based on real data. One method is to calculate the Hildebrand parameters based on surface tension data (Beerbower, 1971) or by monitoring the change of organic layer thickness of intercalated surfactants in different solvents via small-angle neutron scattering (SANS) (Ho et al., 2001).

A method for optical transparent materials like clay is yet missing. Hernandez and Coleman with coauthors have shown a method to measure HSP of graphene (Hernandez et al., 2010), molybdenum disulfide, tungsten disulfide or boron nitride (Coleman et al., 2011). For that, they stressed the dispersions and afterward estimated the concentration of filler in solvents by measuring their optical absorbance. The measured HSP have shown to be useful, and exfoliated flakes were obtained in dispersions with similar HSP.

In this study, a modified version of the Coleman approach is developed. For that four different organophilic mica (OM) have been used, one self-prepared organophilic mica and three commercially available Somasif micas.

The concentration of Somasif mica, which is dispersed in an organic solvent, is measured via gravimetric analysis instead of optical absorption. Concentrations in 10 different solvents have been measured. From those concentrations, the Hansen solubility parameters (HSP) of each OM have been determined. The HSP allows calculating the dispersibility of each Somasif mica in solvents via the Flory-Huggins (F-H) parameter. This F-H parameter describes the extent of interactions in such dispersions and is related to the energy cost of exfoliation (Hernandez et al., 2010). A screening based on F-H parameters identifies suitable solvents to delaminate those OM.

2. Experiment

2.1. Chemicals

Synthetic fluoromicas, namely Somasif™ are supplied by CBC. Co. Non-modified Somasif mica (ME-100), as well as three organophilic Somasif micas, have been used: Somasif MEE, MTE, and MAE. Solvents are supplied by Sigma-Aldrich: acetone, isopropanol (IPA), toluene, tetrahydrofuran (THF), chlorobenzene, *o*-Xylene, propylene glycol methyl ether acetate (PGMEA), isopropyl acetate, cyclohexanone, and chloroform, as well as the surfactants Arquad 2HT-75 (2HT-75). All the materials mentioned above are used as received without further purification.

2.2. Organic modification of Somasif mica

In a 250 ml flask, 1 g of ME-100, was dispersed into 100 ml deionized (DI) water. 1.65 g of 2HT-75 was then added under stirring. After mechanical stirrer overnight, the precipitated organophilic mica (OM) was collected by filtration. Furthermore, the filter cake was repeatedly washed with DI water until no chloride ions could be detected with a silver nitrate solution. 2HT-75 modified Somasif mica (S-2HT-75) was collected.

2.3. Estimation of Hansen solubility parameters

In a 10-ml flask, Somasif mica was dispersed into solvent via an Ultra-Turrax® dispersion instrument. In all experiments 15 mg/ml was used as starting concentration.

The samples were dispersed in solvents at a predetermined speed and time (12.000 rpm for 5 min). After the dispersion step, samples were centrifuged at 2.000 rpm for 5 min. The supernatant was retained for analysis. The Somasif mica dispersibility was defined as the concentration of material remaining after centrifugation. Volumes of 1 ml of this dispersion were filled into Eppendorf tubes. The solvent was then slowly evaporated under vacuum. The solid content was weighed on a micro scale. The concentration/dispersibility of Somasif mica in the dispersion was calculated from this value. Each dispersion was prepared three times, and the mean value of the concentration was used with a standard deviation taken as an estimation of error. All preparations were done at room temperature.

2.4. X-ray diffraction

Wide-angle X-ray-diffraction (XRD) analyses were performed using a Panalytical Empyrean diffraction instrument, a CuKα radiation ($\lambda = 1.542$ Å) and under the operating condition of 40 kV and 40 mA. Scanning was performed in a range of $2\theta = 1°–10°$, with an interval of $0.02°$ and a step time of 10 s.

3. Results and discussion

3.1. X-ray diffraction

Intercalation of surfactants increases interlayer space of clay minerals. This increase of interlayer space is seen as a shift of the X-ray diffraction towards lower 2 theta angles according to Bragg's law. The XRD measurements of Somasif mica in the range of 1° to 10° are shown in Fig. 1 for the four different surfactants. The structures of the used surfactants are shown in Table 1.

The XRD diffractogram of MEE (Fig. 1.MEE) exhibits reflections at 1.8°, 3.7°, and 5.6°, which correspond to interlayer distances of the OM of 4.8 nm, 2.3 nm, and 1.5 nm, respectively. Those variations are related to the surfactant. The used surfactant is quaternary ammonium ion with poly(ethylene glycol) chains (PEG) (Table 1), which varies in it chain lengths. The main reflection and most of the particles have an