Effects of Solvent Solubility Parameters on Organoclay Dispersions

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With Hansen's solubility parameters, $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, the correlation between the degree of exfoliation of organically modified clays and the solvent in which the clay platelets are dispersed/mixed has been analyzed. It has been found that the dispersion force of the solvent, reflected by δ_d, is the principal factor determining whether the clay platelets remain suspended in the solvent while the polar (δ_p) and hydrogen-bonding (δ_h) forces affect primarily the tactoid formation/structure of the suspended platelets. The organically modified clays studied in this work precipitated in any solvent with molecules with moderately strong hydrogen-bonding groups. The correlation found has been used to correctly identify a solvent, trichloroethylene, which completely exfoliates the organically modified clay studied in this work.

Introduction

Recently, nanocomposites composed of clays and polymers have been found to have improved mechanical properties[1−5] as well as enhanced thermal stability.[6] The improved properties are related to the degree of dispersal and exfoliation of the clay platelets in the polymer matrix. Understanding the interaction between organically modified clay (organoclay) platelets and organic solvent molecules as well as the corresponding structure of organoclays in a suspension is a critical step toward tailoring and characterizing nanocomposites formed by organoclays in a polymer matrix. The motivation of this work was, therefore, to explore the correlation between the degree of exfoliation of organoclays and properties of the solvent in which the clays were dispersed by utilizing the corresponding solvent solubility parameters.

Sodium montmorillonite (Na^+−montmorillonite), like all clays, is a crystalline aluminosilicate with a platelet morphology. Each platelet has the 2:1 smectic structure with a middle layer of aluminum hydroxide between two layers of silicon dioxide, possessing a nominal chemical formula of $Na_{0.33}[(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2]\cdot nH_2O$, which varies depending on the source of clay.[7−9] The platelets have a net negative charge and are weakly bound through electrostatic interactions with an interlayer of hydrated cations (Na^+ in the present case). The individual platelets are only 1-nm thick, but have lateral dimensions on the order of 1000 nm. Dry clay particles consist of stacks of platelets, called tactoids. The particles are hydrophilic and readily disassociate in water. Through chemical substitution on the surface, clays of Na^+−montmorillonite can be modified to convert the surface from hydrophilic to organophilic, resulting in organoclays that are dispersible in common organic solvents. Typically, this is accomplished via an organic cationic substitution reaction with the surface sodium ion.[10]

Small-angle neutron scattering (SANS) and wide-angle X-ray scattering (WAXS) are powerful techniques for characterizing microdomains and nanostructures of various polymeric systems as well as particles or fillers in solution or in a polymer matrix. Recently, SANS has been used to study a variety of clay dispersions[11−15] and nanocomposites formed by clays and polymers.[16,17] Our previous SANS and WAXS results[14] demonstrate that

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organoclays (Cloisite 15A (C15A)[18] in that case) dispersed in chloroform were fully exfoliated, whereas they formed tactoids in benzene, toluene, and *p*-xylene, which possess different values of the solvent solubility parameter δ,[19−21] suggesting that the interaction between the organoclay platelets and the solvent molecules might be responsible for the degree of exfoliation of organoclays in dispersion. By following this thought, a series of systematic experiments were undertaken on dispersions of C15A in various organic solvents covering a broader range of δ using the SANS and WAXS techniques.

Experimental Section

C15A, a substituted dimethyl dihydrogenated tallow montmorillonite, used in this work is a commercial product provided as a free-flowing powder by Southern Clay Products, Inc.[18] It is synthesized by ion-exchanging sodium montmorillonite clays with a cation-exchange capacity (CEC) of 1.25 mequiv/g with dimethyl dihydrogenated tallow (di-tallow) ammonium.[22] The di-tallow is a mixture of dimethylammonium surfactants with various carbon chain lengths of ca. 65% of C_{18}, 30% of C_{16}, and 5% of C_{14}.[22,23]

The SANS and WAXS profiles[14] from the dry powders and the dispersions in organic solvents of as-received (unextracted) and of purified (extracted) C15A clays are significantly different, confirming that the organic modifiers (surfactants) are present in excess in the unextracted material as reported by the industrial provider. The scattering data indicate that the swollen tactoids of extracted material in benzene, toluene, and *p*-xylene are thinner, and therefore more numerous, which may account for the bulk suspension behavior. The experimental observations[14] also demonstrate that the extracted material has a stronger tendency to gel.

To remove excess dimethyl di-tallow from the unextracted C15A, the unextracted C15A powders were purified by refluxing with hot ethyl alcohol, which was replaced once daily, for 3 days.[14] The extracted C15A clays were then dried in an oven under vacuum at room temperature for 3 days and dispersed in the solvents listed in Table 1 1% by weight (1 wt %) by sonicating the mixture for 10 min. Dispersions were allowed to reach equilibrium for ca. 1 day under ambient conditions before the SANS and WAXS measurements, which were performed on those dispersions with no visible precipitates.

SANS experiments at room temperature over the q range from 0.004 to 0.442 Å^{-1} were carried out using the 30-m SANS instruments at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR).[24] The scattered intensity was corrected for background and parasitic scattering,[25] placed on an absolute level using a calibrated secondary standard and circularly averaged to yield the scattered intensity, $I(q)$, as a function of the wave vector, q, where $q = (4\pi/\lambda)\sin(\theta/2)$ (θ is the scattering angle). The incoherent background from the pure solvents was measured, corrected by the volume fraction displaced by the dispersed clay, and subtracted from the reduced SANS data. The data points in the q range from ca. 0.35 to 0.42 Å^{-1} were then averaged to yield the estimated incoherent background from the clay in the sample, which was subtracted from the data as well. WAXS measurements were performed at room temperature over the q range from 0.07 to 0.85 Å^{-1} using Ni-filtered Cu Kα X-rays of wavelength $\lambda = 1.54$ Å.

Table 1. Clay Platelet Dispersity of 1 wt % Extracted C15A vs Solvent Solubility Parameters[a−c]

#	solvent	δ_o	δ_d	δ_p	δ_h	H-bonding group	observation
1	pyridine	10.61	9.25	4.3	2.9	strong	precipitates
2	benzaldehyde	10.40	9.15	4.2	2.6	moderate	precipitates
3	benzene*	9.15	8.95	0.5	1.0	weak	tactoids
4	toluene*	8.91	8.82	0.7	1.0	weak	tactoids
5	trichloroethylene	9.28	8.78	1.5	2.6	weak	full exfoliation
6	furan	9.09	8.70	0.9	2.6	moderate	precipitates
7	carbon tetrachloride	8.65	8.65	0	0	weak	tactoids
8	*p*-xylene*	8.80	8.65	0.5	1.5	weak	tactoids
9	chloroform*	9.21	8.65	1.5	2.8	weak	full exfoliation
10	cyclohexanone	9.88	8.65	4.1	2.5	moderate	precipitates
11	cyclohexylamine	9.05	8.45	1.5	3.2	weak	precipitates
12	tetrahydrofuran	9.52	8.22	2.8	3.9	moderate	precipitates
13	cyclohexane	8.18	8.18	0	0	weak	precipitates
14	ethanol	12.92	7.73	4.3	9.5	strong	precipitates
15	acetone	9.77	7.58	5.1	3.4	moderate	precipitates
16	diethyl ether	7.62	7.05	1.4	2.5	moderate	precipitates
17	water	23.50	6.00	15.3	16.7	strong	precipitates

[a] $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ where δ_o = total solubility parameter, δ_d = component due to dispersion forces, δ_p = component due to polar forces, and δ_h = component due to H-bonding. All the solvent solubility parameters are from ref 19 and in units of (cal/cm^3)$^{1/2}$. [b] The solvents are listed in decreasing order of the quantity of δ_d. [c] Asterisk (*) denotes that more details regarding the data can be found in ref 14.

Results and Discussion

On the basis of the concept of cohesive energy, the energy associated with the net attractive interactions of the material, Hildebrand and Scott[26,27] proposed the original definition of what is generally called the solubility parameter: $\delta = (E/V)^{1/2}$, where E is the molar cohesive energy and V denotes the molar volume. This parameter was initially intended for nonpolar, nonassociating liquid (solvent) systems, but the concept has been extended to all types of systems, such as polymer−solvent and polymer−polymer. The unit of δ is (cal/cm^3)$^{1/2}$, and 1 (cal/cm^3)$^{1/2}$ = 2.0455 × 10^3 (J/m^3)$^{1/2}$ = 2.0455 MPa$^{1/2}$. Hansen[28,29] extended the Hildebrand parameter method to polar and hydrogen-bonding (H-bonding) systems, primarily for polymer−solvent interactions, as $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ by assuming that dispersive (δ_d), polar (δ_p), and H-bonding (δ_h) forces act together according to the values of each component measured experimentally via various methods.[19−21]

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Hansen's polar solubility parameter δ_p has been related to the dipole moment μ by Hansen and Skaarup[30] as $\delta_p^2 \sim \mu^2/V^2$, and the Hansen H-bonding parameter δ_h is given by[31] $\delta_h^2 = E_h/V$, where E_h denotes the H-bonding energy. Hansen's total solubility parameter δ_o should be equal to Hildebrand's parameter δ, although the two quantities might be different for materials with specific interactions when they are determined by different techniques.[19−21]

Through the group contribution method, the solubility parameter (δ or δ_o) can be calculated by eq 1.[19−21]

$$\delta_o = \rho \frac{\sum_i F_i}{M} \quad (1)$$

$F_i = (E_i V_i)^{1/2}$, where E_i and V_i are the cohesive energy and the molar volume of the chemical group i being considered, represents the molar attraction constant, which can be found in refs 19 and 21, proposed by Small[32] and is in units of cal$^{1/2}$ cm$^{3/2}$. ρ is the mass density and M is the molar mass of the material. The surfactants on the C15A clay platelet surface are a mixture of dimethyl di-tallow ammonium with various carbon chain lengths of ca. 65% of C_{18}, 30% of C_{16}, and 5% of C_{14},[22,23] which mainly contains $-CH_2-$ and $-CH_3$ groups. The value of F_i is 134 and 189 cal$^{1/2}$ cm$^{3/2}$ for $-CH_2-$ and $-CH_3$ groups,[21] respectively. δ_o for dimethyl di-tallow ammonium of C_{18}, C_{16}, and C_{14} was then estimated to be ca. 9.18, 9.67, and 9.68 (cal/cm^3)$^{1/2}$, respectively. Consequently, the averaged δ_o for the surfactant mixture on C15A was calculated to be ca. 9.35 (cal/cm^3)$^{1/2}$, which falls within the literature range[17] of 8.80−13.69 (cal/cm^3)$^{1/2}$.

The Flory−Huggins interaction parameter[19−21] $\chi \sim (\delta_a - \delta_b)^2$ for binary polymer systems consisting of components a and b, where δ_i is Hansen's total solubility parameter δ_o of species i. The smaller the χ value, the better the miscibility between the components. However, considering only the δ_o value of the solvents given in Table 1 with respect to $\delta_o = 9.35$ (cal/cm^3)$^{1/2}$ calculated for the di-tallow mixture is not sufficient to explain why the extracted C15A clay platelets remained in a solvent such as carbon tetrachloride (#7; $\delta_o = 8.65$ (cal/cm^3)$^{1/2}$) or *p*-xylene (#8; $\delta_o = 8.80$ (cal/cm^3)$^{1/2}$) that yields a relatively large χ value, whereas they precipitated in cyclohexylamine (#11; $\delta_o = 9.05$ (cal/cm^3)$^{1/2}$) or tetrahydrofuran (#12; $\delta_o = 9.52$ (cal/cm^3)$^{1/2}$) in which χ is significantly smaller. To address these issues, solvent properties in detail, mainly involving δ_d, δ_p, and δ_h, should be taken into account.

The solvents studied in this work with their corresponding Hansen's parameters,[19] in units of (cal/cm^3)$^{1/2}$, are listed in decreasing order of the quantity of δ_d in Table 1. Dispersions showing no visible precipitates were characterized by SANS and WAXS to determine the structure of C15A clay platelets in the dispersion as described in ref 14. The results are given in the column labeled "observation" in Table 1. More details

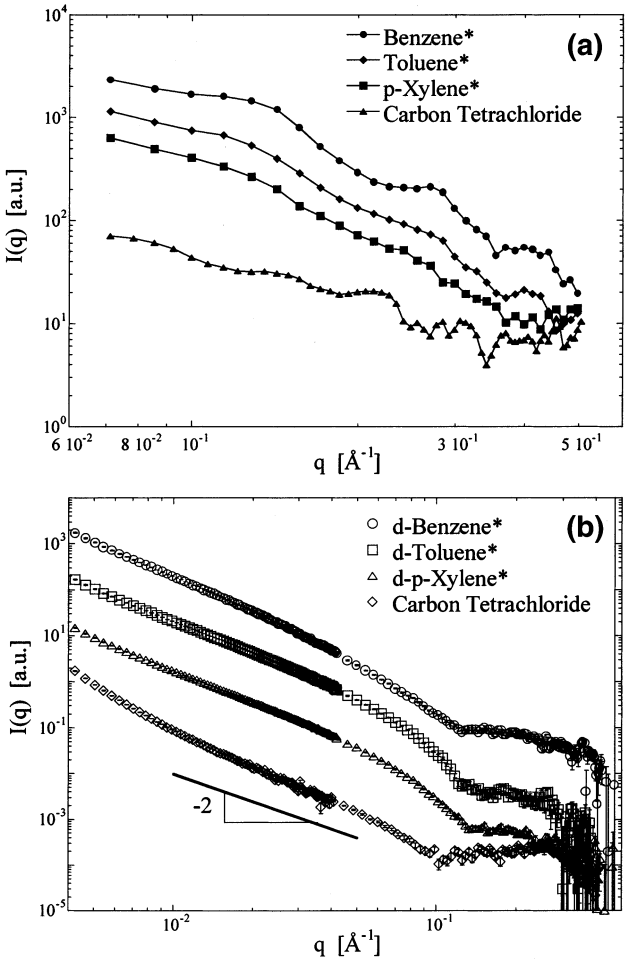

Figure 1. Scattering profiles obtained from the dispersions of extracted C15A clay platelets in benzene, toluene, *p*-xylene, and carbon tetrachloride at 1 wt % by (a) WAXS and (b) SANS. More details regarding C15A platelets in the solvents with a star sign (*) can be found in ref 14. Profiles are vertically offset for clarity.

regarding C15A platelets in the solvents with an asterisk (*) in Figures 1 and 2 as well as in Table 1 can also be found in ref 14. Parts a and b of Figure 1 demonstrate that the extracted C15A clay platelets formed tactoids in benzene, toluene, and *p*-xylene[14] as well as in carbon tetrachloride based on the peaks, reflecting a lamellar (tactoid) structure, seen by WAXS (Figure 1a). This is also reflected in the deviation in slope, which mainly arises from stacking of clay platelets, from the theoretical value of −2 for randomly oriented thin disks in the q range from 0.004 to 0.04 Å^{-1} observed via SANS (Figure 1b).[14] In contrast, the WAXS and SANS data plotted in parts a and b, respectively, of Figure 2 can be directly fit to the single platelet form factor for C15A clay platelets,[14] indicating that the extracted C15A platelets were fully exfoliated (randomly oriented) in chloroform[14] and in trichloroethylene. The solid curve in Figure 2b represents the corresponding model fit to the data. The strong neutron scattering contrast between the deuterated (d-) solvents and the protonated (h-) di-tallow layers, which is absent for X-rays, accounts for the differences observed in the scattering profiles, particularly in the range of $q = 0.1-0.4$ Å^{-1}.

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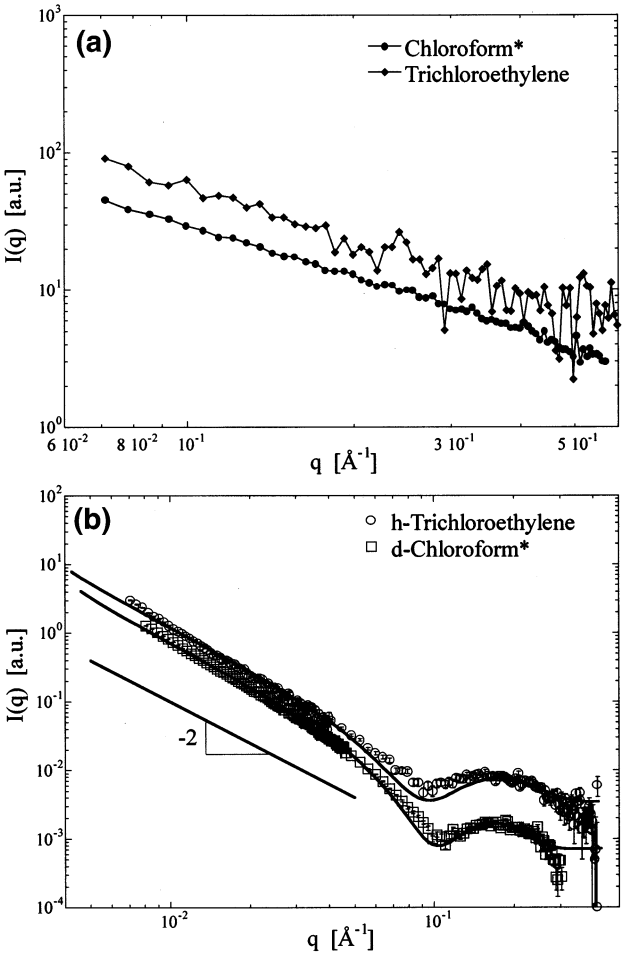

Figure 2. Scattering profiles obtained from the dispersions of extracted C15A clay platelets in chloroform and trichloroethylene at 1 wt % by (a) WAXS and (b) SANS. The solid curve in (b) represents the corresponding model fit to the data. More details regarding C15A platelets in chloroform can be found in ref 14. Profiles are vertically offset for clarity.

In Table 1, the extracted C15A clays precipitated in cyclohexane (#13) but formed tactoids in carbon tetrachloride (#7). Both solvents have only the component δ_d and weak H-bonding groups. In addition, in chloroform (#9) and cyclohexylamine (#11), which possess weak H-bonding groups as well as comparable δ_p, δ_h, and δ_o but different values of δ_d, the platelets were fully exfoliated and precipitated, respectively. It is mentioned earlier in this article that the estimated χ value between C15A and cyclohexylamine (#11) is significantly smaller than that between C15A and carbon tetrachloride (#7), in which the platelets remained and formed tactoids. These observations lead to the conclusion that the dispersion force, reflected by δ_d, is the interaction that determines whether the C15A clay platelets can remain in the solvent. With the same value of δ_d, increasing the values of δ_p and δ_h changes the clay platelet formation from tactoids to complete exfoliation (#7 through #9), indicating that the polar and H-bonding forces of the solvent molecules affect the tactoid formation/structure of C15A in suspension. Nevertheless, if δ_p of the solvent, such as cyclohexanone (#10), is relatively high, even with a larger δ_d value of the solvent, such as pyridine (#1) and benzaldehyde (#2), the platelets precipitate, suggesting that the polarity of the surfactant layer on the clay surface is relatively weak. In contrast, a solvent, trichloroethylene (#5), for instance, with similar quantities of δ_p and δ_h to that of chloroform but a larger value of δ_d would be expected to fully exfoliate the C15A clay platelets as observed. It is noted that any solvent molecules with H-bonding groups stronger than "weak" will precipitate the C15A clay no matter how close the δ_d, δ_p, and δ_h values are to that of chloroform, for example, furan (#6), suggesting that the di-tallow layer on the clay surface possesses relatively weak H-bonding groups.

In addition, in chloroform and trichloroethylene, the values of χ for C15A in these solvents are small. This, perhaps, could partially explain why the extracted C15A platelets were fully exfoliated in chloroform and trichloroethylene, which both possess a quantity of δ_o close to that (9.35 (cal/cm^3)$^{1/2}$) estimated for the di-tallow mixture, when the conditions of δ_d, δ_p, and δ_h as well as H-bonding groups are satisfied.

Conclusions

By utilization of Hansen's solubility parameters, the correlation between the degree of exfoliation of organoclays (C15A) and the solvent in which the clay platelets are dispersed/mixed was successfully analyzed. It was found that δ_d of the solvent is the primary factor determining whether the C15A clay platelets remain suspended, whereas δ_p and δ_h affect the tactoid formation/structure of the platelets in the dispersion. The results suggest that both the polarity and H-bonding groups of the surfactant layer on the clay surface are weak. Consequently, any solvent molecules associated with H-bonding groups stronger than "weak" will precipitate C15A clay. The correlation found has been used to correctly identify a solvent, trichloroethylene, which completely exfoliates C15A clay. The averaged δ_o for the surfactant mixture on C15A was calculated to be ca. 9.35 (cal/cm^3)$^{1/2}$ via the group contribution method. δ_o of the solvent and/or the corresponding χ between C15A and the solvent can be used to estimate/predict the degree of exfoliation of organoclays in a dispersion if the conditions of δ_d, δ_p, and δ_h as well as H-bonding groups are satisfied. Extensive studies on exploring the feasibility of applying the results presented in this article to nanocomposites formed by C15A clays dispersed in selected polymer matrixes are in progress.

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