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The influence of cationic surfactant removal on the thermal stability of organoclays

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Abstract

The microstructure, thermal stability, surface energy and swelling characteristics of two kinds of commercial organoclays, before and after washing treatment with a mixture of H₂O/ethanol, were investigated using X-ray diffraction (XRD), thermogravimetric analysis (TG/DTG), wettability measurement and swelling measurement. This study demonstrates that the external-surface physically adsorbed surfactant can be removed after washing treatment, resulting in an increase in thermal stability and a decrease in surface energy of the resultant organoclays. Organoclays are difficult to be introduced into a solvent when their surface energies are lower than that of the solvent. On the other hand, the organoclay with $\gamma_{\text{organoclay}} < \gamma_{\text{solvent}}$ is easier to be swollen and expandable by the solvent. The swelling and basal spacing measurements of the organoclays introduced into organic media indicate that the swelling factor and the interlayer swelling are two independent parameters. Both the polar character of the solvent and the swelling capacity of clay have a prominent effect on the interlayer swelling of the organoclays.

Keywords: Organoclay; Organic solvent; Surface energy; Swelling factor; Interlayer swelling;

X-ray diffraction; Thermogravimetric analysis

1. Introduction

In recent years organoclays have attracted great attention in a number of applications, such as clay-based nanocomposites [1], absorbents of organic pollutants [2]. More recently, a novel application of organoclays as starting clay materials for preparing clay-based mesoporous materials was reported [3,4].

Organoclays are prepared by modifying clays with cationic surfactants. The most commonly used layer silicates (montmorillonite, hectorite and saponite) in the above mentioned applications belong to the swelling clays (smectite). Because of an isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^+ in the octahedral sheet; Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by cations in the interlayer space. These cations are exchangeable and the sum of their charges is the cation exchange capacity (CEC). This CEC value determines the number of cationic surfactants that can be intercalated into the galleries by ion exchange. Clay minerals are relatively thermally stable compared with organic molecules. These minerals will begin to lose structural hydroxyl groups at ca. 600 °C but will maintain the layer structure up to ca. 900 °C [5]. Clay minerals are hydrophilic and modifying the clay mineral surfaces with cationic surfactants, to convert the normally hydrophilic silicate surface to an organophilic surface, is a strategic step for the above-mentioned applications. All these applications strongly depend on the surface properties and structure of the organoclays. For example, the compatibility between an organoclay and a polymer matrix is the key factor that

determines the structure of the composite as a conventional microcomposite or nanocomposite. The nanocomposite may be classified as intercalated and exfoliated, depending on the degree of dispersion of the clay layers [1].

For synthesis of clay-based mesoporous materials in various organic media, using organoclay as starting clay materials, it is understood that the swelling properties of organoclays will have an important influence on the structure of the resultant materials despite this has not been reported in the literature. This is because, in this case, the interlayer expanding extent of organoclay in organic media controls the entrance of pillaring agents (e.g. silane and their hydrolysis products) and the template height. However, no attention has been paid on this point and the interaction between organoclays and organic media are not well characterized and understood, especially about the correlation between the swelling at macroscopic scale and the interlayer swelling at a nanoscopic scale. The later is of high importance in synthesis of organoclay-based nanocomposites and only a very fewer papers have reported this phenomena. A positive correlation between the swelling volume and the basal spacing were demonstrated when organoclays were introduced into organic media [6,7] whereas Burgentzlé et al. [8] suggested these two parameters were independent.

Another important thing is the stability of surfactant within the organoclay interlayer space in various media, which definitely affects the surface property and structure of organoclay when they are laid in the corresponding media. Previous studies have shown that there are three different molecular environments for surfactants within organoclays: 1) surfactant cations intercalated into the clay

interlayers through cation exchange and bound to surface sites via electrostatic interaction; 2) surfactant (cations and/or molecules) physically adsorbed on the external surface of clay; 3) surfactant molecules located within the clay interlayer [9-16]. Thermal analyses have demonstrated that the decomposition temperature for the surfactants with different molecular environments is different from each other. In other words, the decomposition temperature for the three kinds of surfactants decreases as the order of intercalated surfactant cations, interlayer adsorbed surfactant molecules and external-surface physically adsorbed surfactant. Obviously, an increase of external-surface physically adsorbed surfactant content in organoclays will decrease the thermal stability of organoclays and the resultant composites. However, what is the possible influence of increase or decrease of external-surface adsorbed surfactant content on the surface property and structure of organoclay?

The aim of this work is to investigate the possibility of removing the surfactant within two kinds of widely used organoclays and its influence on the organoclay microstructure and properties. This study provides some new insights into the properties of organoclays and is of importance for applications of organoclays in various fields.

2. Materials and methods

2.1 Materials

Two kinds of widely used organoclay, prepared from 2:1 type swelling clay, were used in this study. Organoclay, Nanofil 15, is prepared by modifying natural

montmorillonite with dimethylammonium, provided by SÜD-CHEMIE Co., Germany. Its formula is $\text{Na}_{0.19}\text{K}_{0.20}\text{Ca}_{0.04}(\text{Mg}_{0.36}\text{Fe}_{0.10}\text{Al}_{1.44})\text{Si}_4\text{O}_{10}(\text{OH})_2$ and the cation exchange capacity (CEC) is 91 meq/100g. The organoclay and the natural montmorillonite (without modification) are denoted as M-1 and M-0, respectively. Another organoclay, SOMASIF MAE, is a kind of synthetic fluorhectorite modified by dimethyl tallow quaternary ammonium ion, provided by CO-OP Chemical Co., Japan. The CEC of synthetic fluorhectorite is 70 meq/100g, and the layer thickness is ca. 0.96 nm. Its structural formula can be expressed as $\text{Na}_{2x}\text{Mg}_{3.0-x}\text{Si}_4\text{O}_{10}[\text{F}_y\text{OH}_{1-y}]_2$, ($x = 0.15-0.5$, $y = 0.8-1.0$). The organoclay and the synthetic fluorhectorite are denoted as H-1 and H-0, respectively.

The two kinds of organoclays, M-1 and H-1, were washed using Soxhlet extraction for 8 hours with a mixture of H_2O /ethanol (25/75 by volume). Then, the washed products were dried at 80°C for 24 hours. The products prepared from M-1 and H-1 are denoted as M-W and H-W, respectively.

As a dispersion medium, four organic solvents (cyclohexane, ethyl acetate, xylene and dimethylsulfoxide) from Aldrich were chosen as function of their solubility parameter, δ_{H} , and surface energy, γ_{LV} , (Table 1). All these solvents have a high purity.

2.2 Swelling measurement

The free swelling factor, S , can be calculated using the following equation:

$$S = (V_s - V_c)/V_c$$

In this equation, V_s is defined as the volume of the slurry while V_c is the volume of

the dry powder [8].

The volume of the slurry (V_s) was measured as follows. 5 grams of organoclays were slowly introduced into a graduated measuring cylinder containing 100 ml of organic solvent. The sediment volume of swollen clay, V_s , was recorded after 24 hours at room temperature. The volume of the organoclay powder (V_c) was gained by the following way: 5 grams of organoclays were loaded into a graduated measuring cylinder. Then, the measuring cylinder containing organoclay was shaken for 5 minutes and the volume recorded.

2.3 Wettability measurement

The sessile drop method was used for the wettability measurement of the organoclays, to determine the hydrophilic or hydrophobic characteristic of these materials. A video camera equipped with a homemade image analysis device allowed the determination, from the shape of the droplet, the contact angle between a given liquid and the surface of organoclay. The reported contact angle was an average value from ten droplets for each treatment of the organoclay surface for a given solvent.

The measurement was performed with distilled water and a dispersive liquid, diiodomethane, in order to determine the surface energy of the organoclays. The dispersive and polar components, and the total surface energy were calculated using Owens-Wendt theory.

2.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was performed in the range of $2-10^\circ$ (2θ) on a Siemens D500 diffractometer equipped with a back monochromator and a copper

cathode as the X-ray source ($\lambda=0.154$ nm). Analyses were performed on both the clay powder and the swollen part taken from the organoclay/solvent suspensions.

2.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a TGA2950 thermobalance. Samples were heated from 30°C to 800°C for M-1 and M-W, and to 950 °C for H-1 and H-W at a heating rate of 10°C/min under helium atmosphere (25 ml/min) in order to evaluate the amounts of physically adsorbed and intercalated surfactants, and their decomposition temperature.

3. Results and Discussion

3.1 Characterization of organoclays

Figure 1 displays the XRD patterns of the two original clays without modification (M-0 and H-0), the two organoclays (M-1 and H-1) and their washed products (M-W and H-W). Comparison of the XRD patterns for the two clays before and after modification indicates that the basal spacings of the clays have been greatly increased after modification. M-1 displays a basal spacing of ca. 27.4 Å while the basal spacing of M-0 is 11.7 Å. The montmorillonite sheet thickness is 9.7 Å, and the estimated interlayer height of M-1 is ca. 17.7 Å, indicating a paraffin-monolayer arrangement of the intercalated surfactants [17,18]. The diffraction peaks for both M-0 and M-1 are broad and low intensity, reflecting poor crystallinity of the montmorillonite. For H-1, two doublets appear at 30-34 and 17-20 Å, respectively, indicating a heterogeneous structure in H-1. This results from the different surface

charge density of clay layers, similar to that in our recent study of organoclay prepared from a special Wyoming montmorillonite [19].

Both the DTG curves of H-0 and M-0 display two peaks at 47 and 901 °C for H-0 and at 62 and 625 °C for M-0 (Fig. 2), corresponding to the loss of the physically adsorbed water and dehydroxylation of clay, respectively. As shown by the TG curve of H-0, there is not any mass loss during 200 – 600 °C. This means that H-0 does not undergo any thermally induced changes in this temperature range. However, for M-0, there is a slight mass loss in the range of 200 – 500 °C, possibly corresponding the loss of the hydrated H₂O (ca. 1 wt.%) within the interlayer space [20]. TG curves of H-1 and M-1 (Fig. 2) show that there is ca. 34.5% and 40.1% (wt%) of organics in M-1 and H-1, respectively. Both the DTG curves of H-1 and M-1 display three peaks in the temperature range of 200-450 °C. The peaks at 300-450 °C correspond to the evaporation and decomposition of the intercalated surfactants while the peak at 272 °C for H-1 and 265 °C for M-1 to those of the physically adsorbed surfactants [10,14,16].

However, after washing treatment with a mixture of H₂O/ethanol, both the resultant products show prominent changes in the interlayer structure and the thermal property as indicated by the X-ray diffraction and thermogravimetric analysis. XRD pattern of M-W (Fig. 1) displays the basal spacings at 24.2 Å, indicating a significant decrease of the basal spacing when compared with that of M-1. For H-W, a regular (001) reflection ($l = 1, 2, 3, \dots$) with high intensity appears in the XRD pattern with the basal spacing at ca. 28.5 Å instead of the occurrence of doublet peaks in that of

H-1, indicating a homogeneous structure existing in the washed products. This results from the dissolution of the physically adsorbed surfactants and “rearrangement” of the intercalated surfactants. This concept is supported by the thermogravimetric analysis. Comparison of the DTG curves of H-1 and M-1 before and after washing treatment demonstrates that the peaks at ca. 265 °C for M-1 and 272 °C for H-1, corresponding to the external-surface physically adsorbed surfactants, do not appear in the DTG curves of the washed products. The peaks at 300 - 450 °C in the DTG curves of M-1 and H-1, corresponding to evaporation and decomposition of the intercalated surfactants [10,14,16], shift to higher temperature in the DTG curves of the washed products. In addition, TG curves show that the surfactant quantity in the organoclays decreases to 30.2% (M-W) and 36.4% (H-W) from 34.5% (M-1) and 40.1% (H-1), respectively. These prominent changes reflect that the external-surface physically adsorbed surfactants are removed away during the washing treatment and the well-intercalated surfactants show a higher thermal stability [8,21].

To elucidate the change of surface property for organoclays after washing with a mixture of H₂O/ethanol, the surface energy, energy of polar component and energy of dispersive component of M-1 and M-W were determined by a wettability measurement (shown in Table 2), using the sessile drop method. Unfortunately, it is impossible to make a disk for measuring the surface energy of H-1 and H-W. As shown in Table 2, it can be seen that both the polar and dispersive components of the organoclay decrease after washing. Consequently, its total surface energy decreases. This demonstrates that the removal of external-surface physically adsorbed

surfactants lead to a decrease of surface energy of the organoclay.

3.2 Swelling measurement and basal spacings in organic solvents

The possibility of introducing organoclays into the organic solvents strongly depends on the solubility parameter and surface energy of the solvents. Table 1 displays solubility parameters and surface energies of the solvents used in this study, and the surface energies of M-1 and M-W are shown in Table 2. During the introduction of organoclays and the washed products into solvents, it can be found that these organoclays are easier to be introduced into the solvents with lower surface energy, cyclohexane and ethyl acetate, and lead to the formation of a gel. When introducing these samples into xylene, with a higher surface energy, a very slow sediment happens and a gel is formed. However, these samples are difficult to be introduced into dimethylsulfoxide, which has much higher surface energy than other three solvents used in this study, and all organoclay samples are retained over the solvent. Only after shaking, these samples are settled and lead to the formation of a gel. Two phases are present in the measuring cylinders: one is a slurry composed of organoclay and solvent, and the other phase is only pure solvent without clay. Here, it can be found that when the surface energy of the solvent is close to or higher than that of organoclay, i.e., $\gamma_{\text{solvent}} \cong \gamma_{\text{organoclay}}$, it is difficult to introduce the organoclay into the solvent whereas the organoclay with $\gamma_{\text{organoclay}} > \gamma_{\text{solvent}}$ is easier to be introduced into the solvent.

Figure 3 displays the swelling factors for organoclays and the washed products in different organic solvents as a function of the solvent surface energy and solubility

parameter, respectively, indicating that the swelling factors for the organoclays strongly depend on the characteristics of the organoclays and the solvents. Generally, M-1 and M-W have bigger swelling factors than that of H-1 and H-W except in cyclohexane. The swelling factors of H-1 and H-W strongly depend on the solubility parameters, i.e., the swelling factors decrease with the decrease of the solubility parameter of the organic solvents (Fig. 3). However, this kind of relationship does not exist between M-1, M-W and the organic solvents. For M-1 and M-W, the aromatic solvent (xylene) and ethyl acetate are the better swelling agents than cyclohexane and dimethylsulfoxide.

Figure 4 displays the basal spacings for organoclays and the washed products in different organic solvents as a function of the solvent surface energy and solubility parameter, respectively. Generally, it can be seen that the basal spacings of H-1 and M-1 in the organic solvents are larger than those of H-W and M-W, and the variation between the basal spacings of H-1 and H-W is more obvious than that between M-1 and M-W. Compared with the basal spacing of M-1, M-1 loaded in the solvents of cyclohexane, ethyl acetate and xylene, respectively, has a prominent d_{001} decrease (Δd_{001}), which reaches 4-5 Å. This might result from the dissolution of the physically adsorbed surfactants as discussed previously. However, when M-1 is introduced into dimethylsulfoxide, the XRD pattern shows a significant Δd_{001} increase of ca. 4 Å. For M-W loaded in the solvents of cyclohexane, ethyl acetate and xylene, a slight increase of the basal spacing (Δd_{001} is no more than 2 Å) is recorded while an increase of Δd_{001} in dimethylsulfoxide reaches 9 Å. Similar changes are also recorded when H-1 and

H-W are introduced into the same organic solvents. In addition, when H-1 is loaded in the organic solvents, two single peaks, instead of the doublet peaks at 30-34 and 17-20 Å (not shown), are recorded, indicating that the heterogeneous structure in H-1 has been transferred into a homogenous structure. This kind of structural transformation also should be attributed to the dissolution of the physically adsorbed surfactants and reorganization of the intercalated surfactants, similar to the case of H-1 washed with the mixture of H₂O/ethanol. In dimethylsulfoxide, the basal spacing increase (Δd_{001}) for H-W is about 5 Å, less than that for M-W (ca. 9 Å). Interestingly, despite of the prominent basal spacing difference between the two groups of organoclay (M-1, M-W and H-1, H-W) in the organic solvents of cyclohexane, ethyl acetate and xylene, they show similar basal spacings (33-35 Å) in dimethylsulfoxide (Fig. 4). This phenomenon is in agreement with the experiments performed by Moraru [6] and Burgentzle et al. [8].

The basal spacing measurement indicates that the most effective solvent for d_{001} increase is dimethylsulfoxide, which has the largest polarity. The polarity of the solvent has dispersion aid for the increase of the basal spacing. This means the polar character of the solvent is a key parameter for interlayer swelling of the introduced organoclay [8]. In addition, a slight increase of the basal spacings of the organoclays in cyclohexane, ethyl acetate and xylene results from the insert of solvent molecules into the clay interlayer. The insertion action strongly depends on the compatibility between the relative surface energies of solvent and organoclay.

However, our swelling measurement demonstrates that the largest swelling factor

for M-1 and M-W is in the solvent xylene and that for H-1 and H-W is in the solvent cyclohexane. Integration of the swelling and basal spacing measurements indicates that the swelling factor (S) and the basal spacing variation (Δd_{001}) are two independent parameters. The gel results from the percolation of stacked platelets in tactoids, keeping the initial interplatelet distance to form a macrogel [22], rather than from the expansion and exfoliation of clay platelets [7]. Furthermore, it is believed that the interlayer swelling of organoclays depends not only on the physical-chemical properties of organic solvents and the surfactants but also the property of the clay minerals. The experiment about grafting silane onto M-0 and H-0 under identical conditions has demonstrated that M-0 has better expanding capacity than H-0 does [20], in which it was reported that the basal spacings for the silane grafted samples from M-0 and H-0 are 17.7 and 14.5 Å, respectively. This can well explain that the basal spacing of H-1 and H-W is always bigger than that of M-1 and M-W when $\gamma_{\text{organoclay}} > \gamma_{\text{solvent}}$.

4. Conclusions

This study demonstrates that the external-surface physically adsorbed surfactant can be removed after washing with a mixture of H₂O/ethanol. This will lead to increase the thermal stability of the resultant organoclays but decrease the surface energy. When the surface energy of the solvent is close to or higher than that of organoclay, i.e., $\gamma_{\text{solvent}} \cong \gamma_{\text{organoclay}}$, it is difficult to introduce the organoclay into the solvent. On the other hand, the organoclay with $\gamma_{\text{organoclay}} < \gamma_{\text{solvent}}$ is easier to be

swollen and expandable by the solvent. The measurements of swelling and basal spacing indicate that the swelling factor is independent from the increase of basal spacing. The biggest basal spacing was observed in dimethylsulfoxide for all samples, which has the largest polarity. The polar character of the solvent and the swelling capacity of clays have an important influence on the interlayer swelling of the introduced organoclay.

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Table 1

Solubility parameters and surface energies of the solvents used in this study

Solvent	Solubility parameters ($\delta_H(\text{MPa}^{0.5})$)	Polarity index (a.u.)	Surface energy ($\gamma_{l/v}$ ($\text{mN}\cdot\text{H}^{-1}$))
Cyclohexane	0.2	0.2	25.5
Ethyl Acetate	5.1	4.4	23.9
Xylene	3.1	2.5	30.1
Dimethylsulfoxyde	10.2	7.2	36

Table 2

The surface energy and its polar and dispersive components of M-1 and M-W

Sample	Polar Component (mJ/m^2)	Dispersive Component (mJ/m^2)	Total (mJ/m^2)
M-1	6.4	29.6	36.0
M-W	3.6	28.5	32.1

Figure Captions

Figure 1 XRD patterns of the two original clays (M-0 and H-0), the two organoclays (M-1 and H-1) and their washed products (M-W and H-W).

Figure 2 TG and DTG curves of the two original clays (M-0 and H-0), the two organoclays (M-1 and H-1) and their washed products (M-W and H-W).

Figure 3 The swelling factors for organoclays and the washed products as a function of the solvent surface energy (a) and solubility parameter (b).

Figure 4 The basal spacings for organoclays and the washed products as a function of the solvent surface energy (a) and solubility parameter (b).

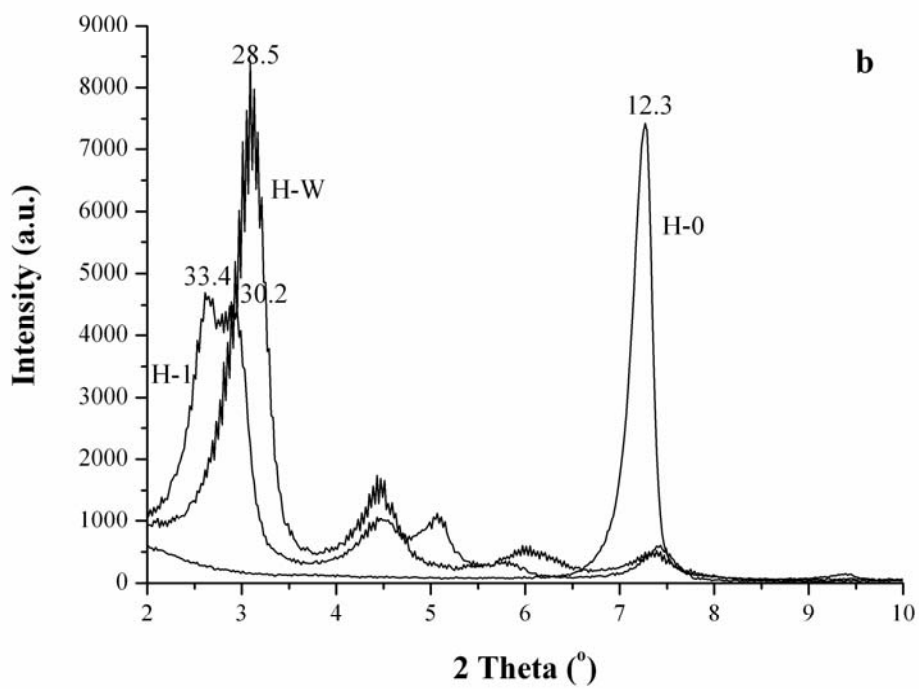
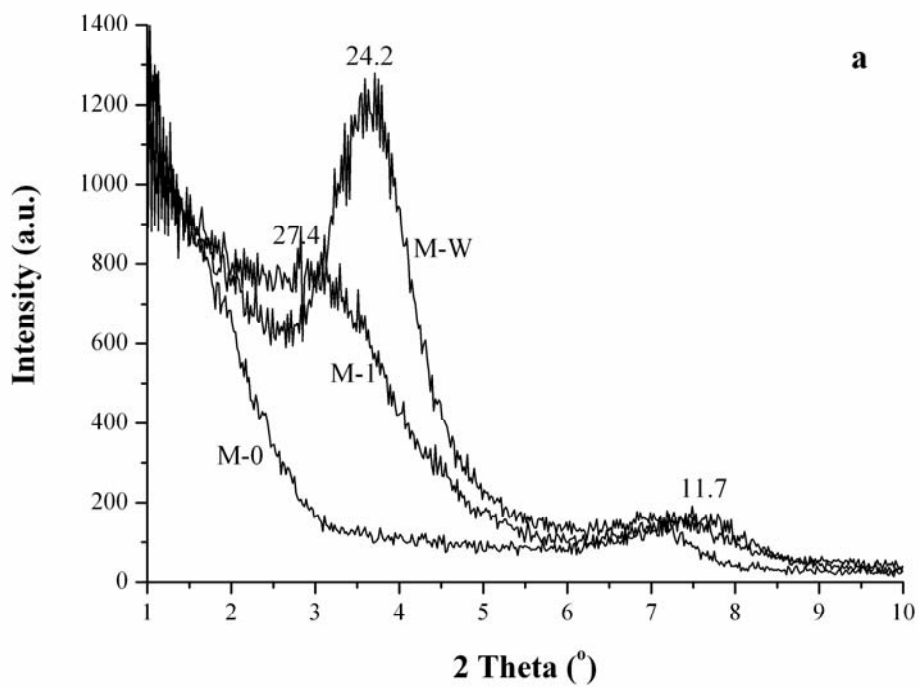


Figure 1

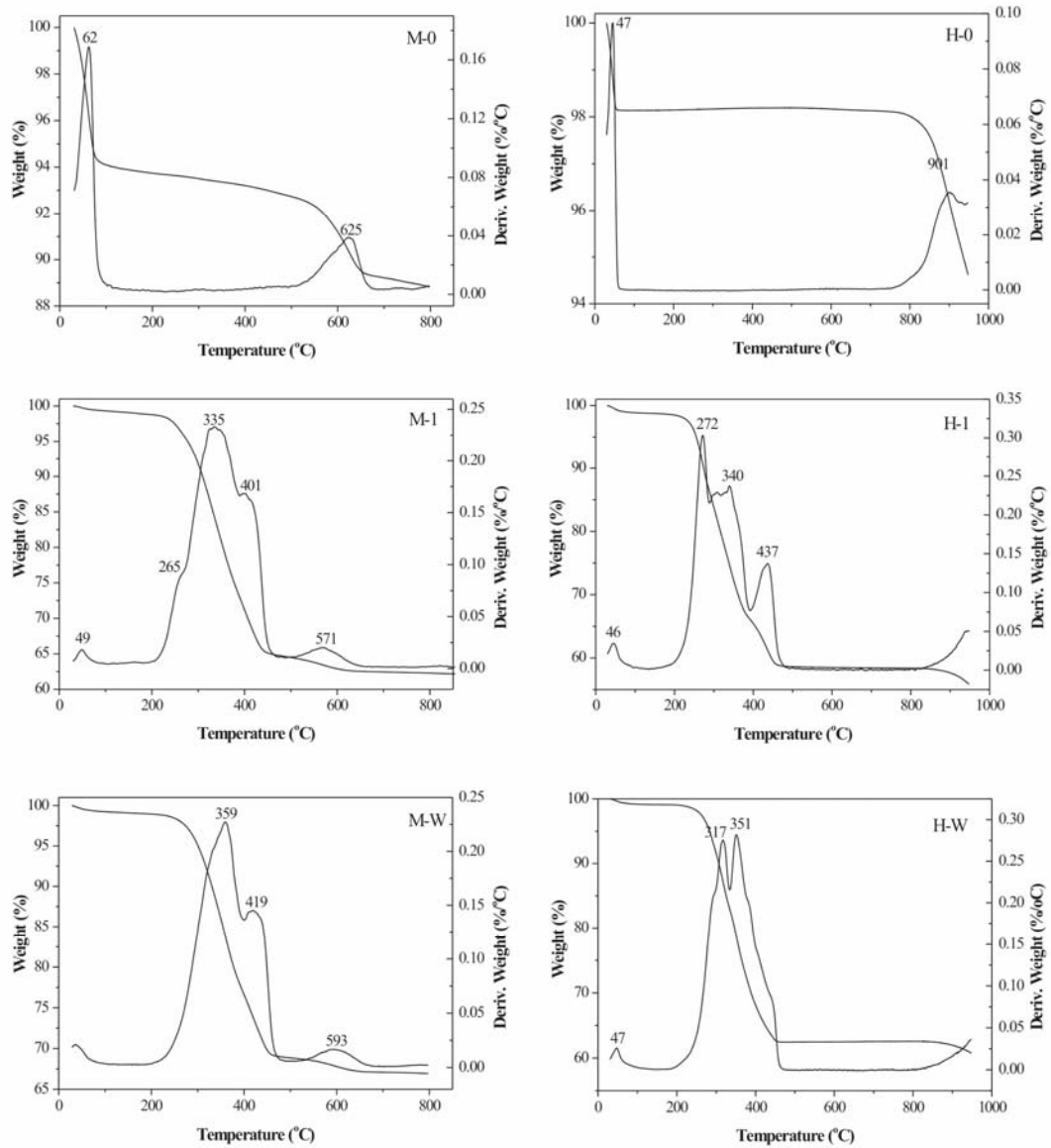


Figure 2

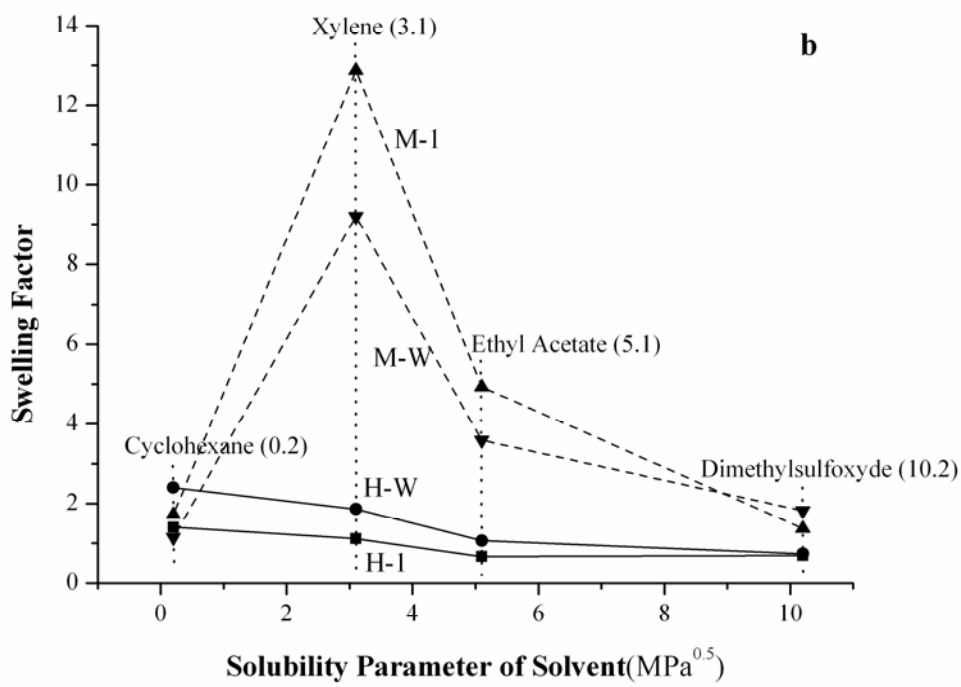
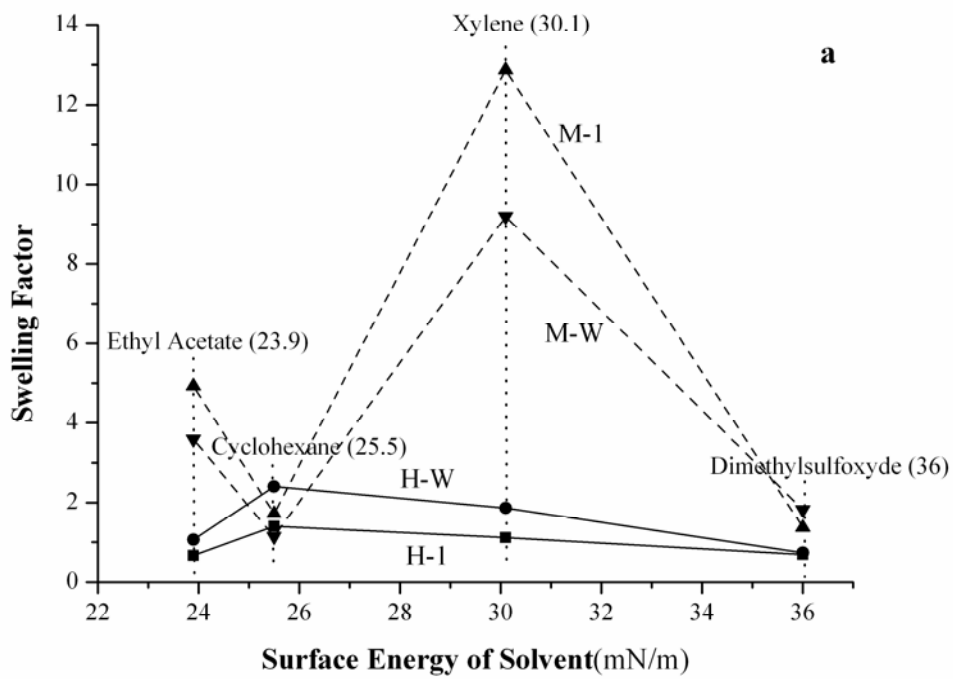


Figure 3

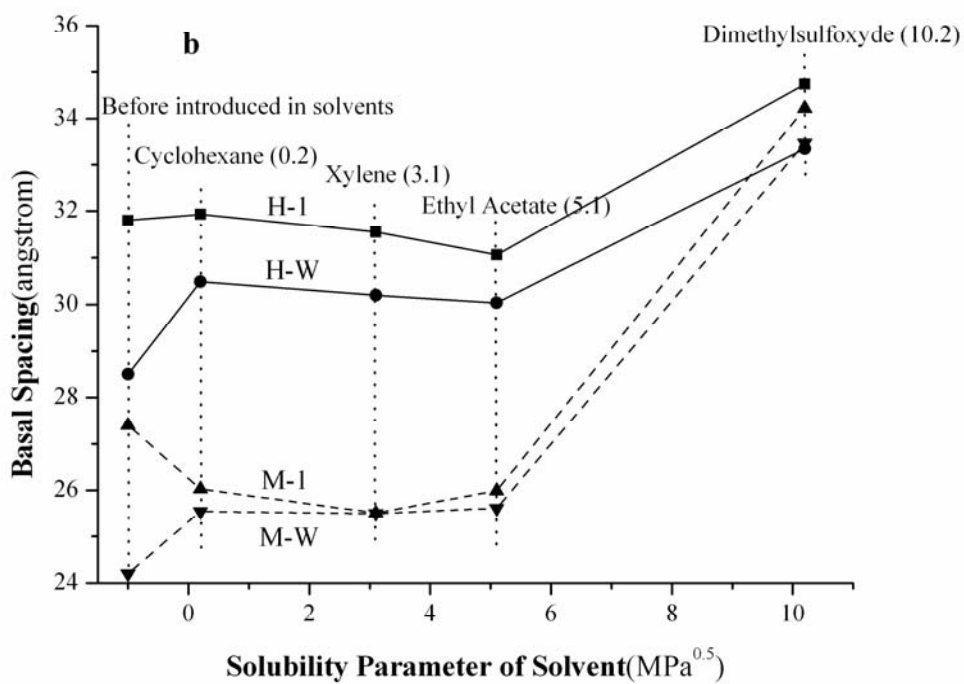
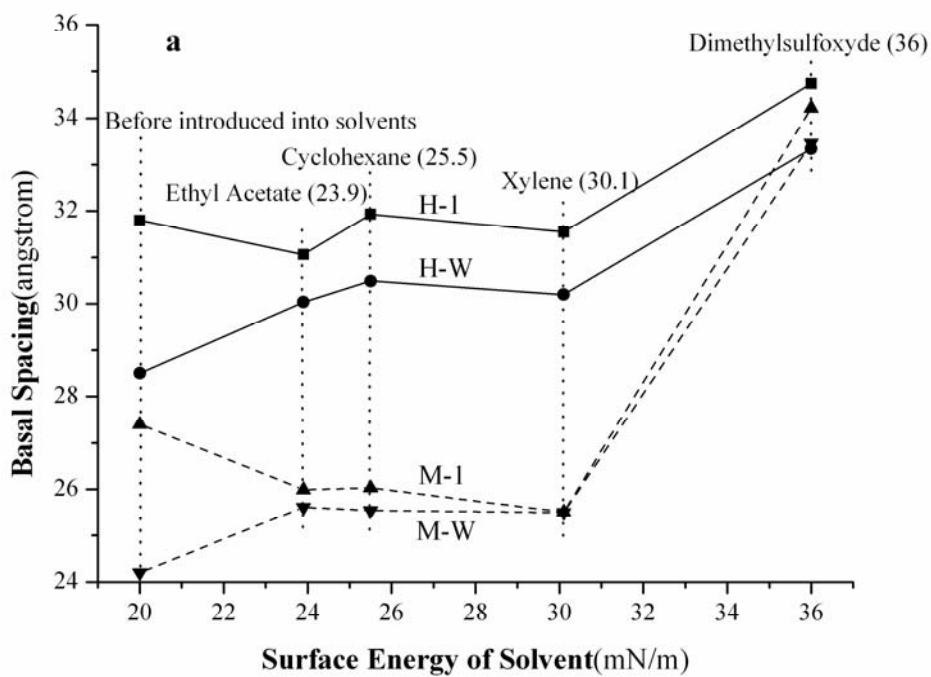


Figure 4