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Solution intercalation of polystyrene and the comparison with poly(ethyl methacrylate)

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Abstract

Polystyrene nanocomposites have been prepared via solution intercalation method. Combination of wide-angle X-ray diffraction and thermogravimetric analysis is used to study the effect of solvents on the morphology of the nanocomposites as a function of the amount of residual solvent. *d*-Spacing of the polystyrene nanocomposites has a minimum value when the residual solvent concentration is between 2 and 4 wt%. Different interaction level between the solvent molecules and polymer chains is considered to be the reason for this special *d*-spacing change behavior. By comparing the solution intercalation of polystyrene and poly(ethyl methacrylate) from different solvents, it is concluded that the interactions between polymer–surfactant, solvent–surfactant, and polymer–solvent play important role for the solution intercalation of polymers.

Keywords: Polystyrene; Polymer–solvent interaction; Nanocomposites

1. Introduction

Nanocomposites have attracted attention of researchers in the past 10 years, in part, by the realization that nanoscale materials often exhibit unique physical and chemical properties. The ultrafine phase dimensions of nanocomposites, typically ranging between 1 and 10 nm, lead to new and improved properties when compared to their pure polymer constituent or their microcomposite counterparts. For example, polymer-silicate nanocomposites exhibit increased modulus [1–3], decreased thermal expansion coefficient [4,5], reduced gas permeability [6,7], increased solvent resistance [8], and enhanced ionic conductivity when compared to pristine polymers [9,10].

The preparation method of nanocomposites can be classified into three categories according to starting materials and processing techniques: intercalation polymerization, which includes the intercalation of one or more suitable monomers and subsequent polymerization [11–14]; polymer intercalation by the solution method [15–17]; and polymer intercalation by the melt method [18–19]. Solution intercalation method has been employed either for water soluble polymers, such as polyvinyl alcohol [15], and poly(ethylene oxide) (PEO) [16], and hydrophobic polymer systems such as high density polyethylene (HDPE) [17]. Melt intercalation has great advantages because the absence of organic solvent is environmentally benign, and the ability to adopt processing techniques like extrusion and injection molding. On the other hand, solution intercalation method involves the use of large amount of organic solvents, which is usually environmentally unfriendly; therefore, it is not an ideal way to prepare commercial nanocomposites. However, since the solution method gives a good control on the homogeneity of constituents, it helps to understand the intercalation process and nanocomposite morphology. It also leads to a better understanding of the structure and dynamics of the intercalated polymers in these nanocomposites, which can provide molecular insight and lead to the design of materials with desired properties. Therefore, in this study, the solution intercalation process is used as the nanocomposite preparation method to understand the polymer–solvent, polymer–surfactant, and solvent–surfactant interaction effects, and the intercalation process.

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2. Experimental

2.1. Materials

The montmorillonite, Bentolite-L, was supplied by Southern Clay Products, with a cation-exchange capacity (CEC) of 80 mequiv./(100 g). Hexadecylamine with purity of 98% was purchased from Aldrich Chemical Co. and was used as received. Polystyrene (PS) and poly(ethyl methacrylate) (PEMA) were also purchased from Aldrich Chemical Co., with a weight average molecular weight of 125,000–250,000 and 550,000, respectively. Tetrahydrofuran (THF), methyl ethyl ketone (MEK), ethyl acetate, toluene, ethyl ether, methyl chloride, dioxane, and ethanol, all from the Aldrich Chemical Company with purity better than 99%, were used as received.

2.2. Instruments and methods

2.2.1. Preparation of organoclay

Organophilic montmorillonite was prepared by reacting original clay with hexadecylamine with the cation exchange method following Ref. [20]. In brief, hexadecyl ammonium chloride solution was prepared by adding stoichiometric amount of hexadecylamine and HCl solution into 80 °C water. After the addition of clay, the system was stirred at 80 °C for 6 h. The resultant precipitate was collected by suction filtration and washed by 80 °C water at least three times. The precipitate was then dried at 120 °C in a vacuum oven for 48 h and the final product is designated as organoclay.

2.2.2. Preparation of nanocomposites

For solution intercalation, mixtures of polymer and solvent were stirred at elevated temperature for 1 h to obtain homogeneous solutions. Different amounts of organoclay were added to the clear solutions and the suspensions were stirred at 80 °C for 8 h. The dispersed clay systems were then cast into aluminum pans. The solvents were first evaporated at room temperature for two days and then dried in a vacuum oven at room temperature. The samples were heated to 50 °C in the vacuum oven in order to further dry the solvent when the solvent content became approximately 5 wt%.

Melt intercalation was undertaken as follows. Particles of polymer and silicate with the desired polymer-to-organoclay weight ratios were roughly mixed using a spatula before being fed into a twin-screw extruder, Microcompounder from Daca Instruments, Inc. The mixing time was 10 min at 190 °C with a speed of 100 rpm. Polymer concentration is expressed as the weight percentage of polymer over total weight (g/g).

2.2.3. Instruments

Wide-angle X-ray diffraction was performed by a Philips XRG 3100 diffractometer with Cu Kα radiation, using a scanning speed and step size of 0.06°/min and 0.01°, respectively. The data analysis is done with a commercial software (Grams 32) from Galactic Inc. The amount of residual solvent is obtained from thermogravimetric analysis (TGA), from the weight loss at 250 °C, which was performed with Hi-Res TGA model 2950 from TA instruments. The evaporation temperature is determined as the peak value of derivative temperature of the TGA weight loss thermogram.

3. Results and discussion

Polymer intercalation into the silicate galleries from solution has been recognized for nearly a century [21]. The preparation of polystyrene–clay nanocomposites has been reported through almost all the nanocomposite preparation methods known, like bulk polymerization intercalation, solution polymerization intercalation, emulsion polymerization intercalation and melt blending methods. However, it was reported that polystyrene–clay nanocomposites are inaccessible by solution intercalation techniques and the attempts to intercalate PS into the same organosilicate from solution (toluene) resulted in the intercalation of the solvent instead of the polymer [22]. Therefore, the first stage in this study is to demonstrate the intercalation of polystyrene through the solution method.

Fig. 1 compares the X-ray diffraction patterns of original organoclay, polystyrene composite prepared by the solution method with PS concentration at 90 wt%, and organoclay that went through the same solution preparation process without the presence of polystyrene. Toluene is used as the solvent in this solution preparation method. The organoclay has a diffraction angle at $2\theta = 5°$ with a d-spacing of 1.77 nm, indicating that the clay galleries are expanded by 0.77 nm with the intercalation of hexadecylamine. Stirring

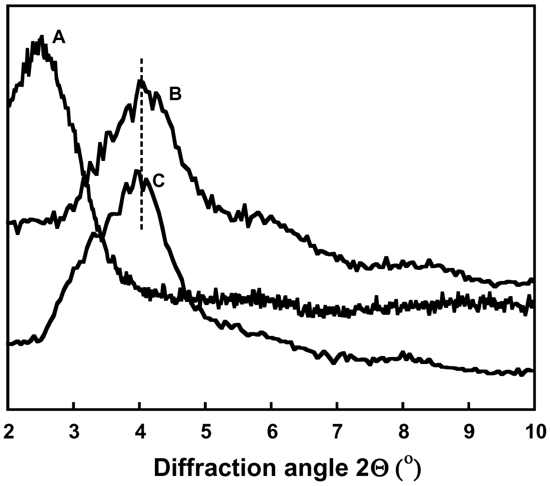

Fig. 1. Comparison of the X-ray diffraction curves of (A) mixture of organoclay and polystyrene (90 wt% PS) treated from toluene, (B) organoclay treated from toluene, and (C) organoclay.

of organoclay in hot toluene resulted in good expansion of clay galleries, which yielded a good homogeneous system. However, the completely dried organoclay after toluene treatment has exactly the same diffraction pattern as the original organoclay, which indicates that the solvent treatment did not change the organoclay morphology. For the system with polystyrene, the X-ray diffraction angle of the completely dried sample changed to 2.8°, meaning a *d*-spacing increment of 1.38 nm compared to the organoclay. These results prove that it is the polystyrene rather than the solvent that intercalates into the silicate layers by the solution intercalation method.

Fig. 2 shows the *d*-spacing increment of the polystyrene nanocomposites from both the solution and melt intercalation methods as a function of polystyrene concentration. The results for solution intercalation method are obtained after the completely dried sample was annealed at 165 °C for 6 h in order to reach the thermodynamically equilibrium state. It is clear that the *d*-spacing increment of the polystyrene nanocomposites via melt intercalation method increases gradually with polystyrene concentration up to 40 wt%, after which it stabilizes at 1.17 nm. However, the situation is different for the results from the solution intercalation method. The *d*-spacing increases drastically to about 1.17 nm when polystyrene concentration is above 10 wt% and this *d*-spacing increment does not change when polystyrene concentration increases further. The level-off *d*-spacing increment is the same as the value obtained from the melt intercalation method at high polystyrene concentration range. However, the *d*-spacing does not show much change compared to the organo clay in the low polystyrene concentration range, which is below 10 wt%. It appears that a critical polystyrene concentration is required, in order for the intercalation of polystyrene into the silicate galleries via solution intercalation method to take place. This phenomenon is the same for all other solvents studied in this paper, like ethyl acetate, tetrahydrofuran, methyl ethyl ketone, dioxane, and carbon disulfide. When the polystyrene concentration is below 10 wt%, no *d*-spacing change is observed compared to the organoclay. Only when polystyrene concentration is above 10 wt%, the completely dried sample shows a *d*-spacing increment. Although it is possible that the intercalation may not cause the *d*-spacing change in all cases, the *d*-spacing of the specific organoclay used in this study indicates that the orientation of amine chains within the silicate galleries should be parallel to the silicate layers [23]. Hence, we would imagine that further intercalation of polymer chains should cause the *d*-spacing increment, which is the case for the melt intercalation method. Accordingly, for solution intercalation of polystyrene, with polystyrene concentration below 10 wt%, no intercalation takes place for all the solvents used.

Although the *d*-spacing increment of polystyrene nanocomposites does not change as a function of polystyrene concentration, the morphology of the silicate galleries does change when polystyrene concentration increases. In the Bragg's equation, $2d \sin\theta = \lambda$, the d provides the information of basal *d*-spacing, while λ is the wavelength and θ is the basal diffraction angle. In the equation $d' = \lambda/\beta \cos\theta$, the d' provides the information of the crystal size, while λ is the wavelength, θ is the basal diffraction angle, and β is the full width at half maximum height of the basal diffraction peak (in radian unit) [24]. Therefore, the d'/d from the X-ray diffraction results can provide us the information of the ordering of the silicate galleries, i.e. the number of orderly stacked silicate layers, which is expectedly an average result. Fig. 3 shows the results of the ordering of completely dried solution-prepared polystyrene nanocomposites as a function of polystyrene concentration. For composite with 10 wt% of polystyrene, since no intercalation of polystyrene happens, the organoclay in the composite has similar ordering as the original clay. The intercalation of polystyrene increases the *d*-spacing of the silicate gallery. At the same time, the breadth of the basal diffraction peaks increases, suggesting a

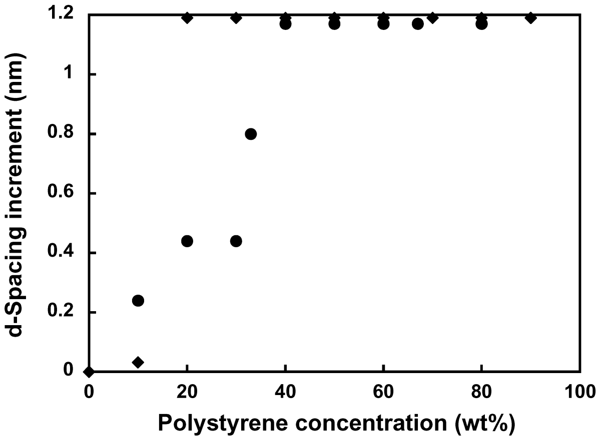

Fig. 2. Gallery size of polystyrene nanocomposites from both of the solution intercalation (toluene as the solvent) (◆) and melt intercalation (●) methods as a function of polystyrene concentration.

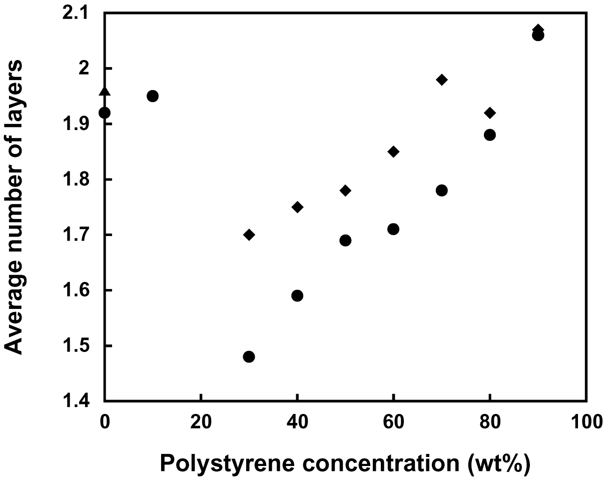

Fig. 3. Concentration dependence of ordering of the silicate layers in (●) PS nanocomposites from solution, (◆) PS nanocomposites annealed at 165 °C for 6.5 h, and (▲) original organoclay.

very broad distribution of the layered structure. Besides, the ordering of clay layers decreases compared to the organoclay upon the initial polymer intercalation. It is possible that the intercalation of small amount of polystyrene opens up the edge of the silicate layers and destroys the parallel structure of the silicate gallery; therefore, the ordering of polystyrene intercalated clay has lower ordering than the original organoclay. Further addition of polystyrene would not cause further increase of *d*-spacing. Instead, the further intercalated polystyrene molecules would enter the already opened silicate galleries, resulting in more ordered clay structure. Results also show that, after further annealing of the polystyrene nanocomposites above polystyrene's glass transition temperature, the ordering of the clay is improved. This can be explained as the consequence of internal structure rearrangement.

In order to understand the role of solvent on the polymer solution intercalation process, the drying process of the air dried, cast films of polystyrene–clay nanocomposites were tracked by X-ray diffractometer for *d*-spacing changes. TGA was used to examine the amount of the residual solvent and its evaporation temperature on the identical samples used for the X-ray analysis. Fig. 4 shows the *d*-spacing dependence on the amount of residual solvent. Four different solvents with different boiling temperature and polarity were used in this study. Some related physical parameters of the solvents are compared in Table 1. Independent of the solvent type, *d*-spacing changes show a similar trend as the amount of residual solvent changes. The *d*-spacing first decreases continuously, then, after reaching a minimum as more solvent evaporated, the *d*-spacing increases within a certain range of residual solvent concentration, until the nanocomposites are totally free of solvent.

The appearance of a minimum *d*-spacing for the polystyrene nanocomposites when the solvent concentration is between 2 and 4 wt% is an unexpected phenomenon, though it is very similar to the antiplasticization phenomenon. The different states of the interaction between polymer chain and solvent molecules are proposed to explain this phenomenon. One state is that the solvent molecules have weak interaction with the polymer chains. This type of solvent dominates the system when the solvent concentration is high. The evaporation of these weakly interacting solvent molecules results in the shrinkage of the polymer chain, leading to a *d*-spacing decrement. The other state is that the solvent molecules have strong interaction with the polymer molecules. This type of interaction dominates when the solvent concentration is low. These strongly interacting solvents restrict the mobility and conformational freedom of the polymer chains. They also restrain the polymer molecules from reaching the thermodynamic equilibrium significantly. Release of the strong interaction frees the polymer chain. Therefore, the *d*-spacing of clay layer increases as the strongly interacting solvent molecules are released. The polymer chain size is smaller in the presence of such solvent than the one without solvent in the confined space and the difference in the size is solvent dependent. This *d*-spacing change process is schematically shown in Fig. 5.

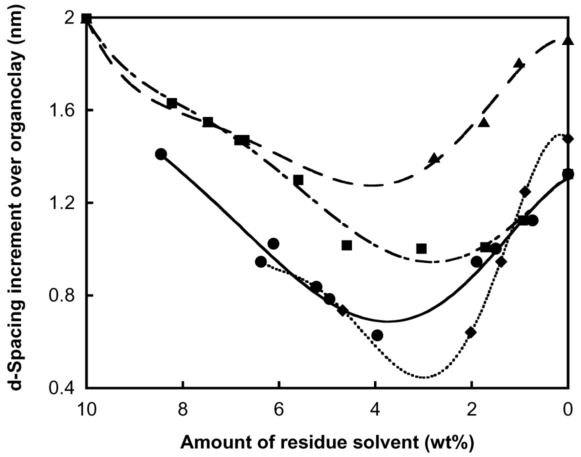

Fig. 4. *d*-Spacing change of the polystyrene–clay cast film as a function of residual solvent content (●) methyl ethyl ketone, (▲) THF, (■) toluene, and (◆) ethyl acetate.

Solution intercalation method is considered as a two-stage process; however, two different intercalation mechanisms are involved: exfoliation-adsorption solution intercalation [25] and exfoliation-exchange solution intercalation [26]. It is well known that the weak dipolar or van der Waals forces between the silicate layers make the silicate layers easy to be separated by the solvent molecules. The stacks of silicate layers are exfoliated into single layers by the solvent. For exfoliation–adsorption intercalation mechanism, the polymer dissolves in the solvent then adsorbs onto the delaminated silicate sheets. When the solvent is evaporated, the sheets reassemble, sandwiching the polymer and residual solvent molecules to form the intercalated structure. For the polymer–solvent exchange mechanism, polymer is exchanged with the intercalated solvent in the gallery. Therefore, the driving force for polymer intercalation into layered silicate from solution is the entropy gained by desorption of solvent molecules, which compensates for the entropy decrease of the confined, intercalated chains. In this case, intercalation occurs only for certain polymer/solvent pairs via solution intercalation. Judging from the phenomenon that the *d*-spacing shows a continuous decrease when more solvent evaporates and *d*-spacing change shows a similar trend for different solvents, exfoliation–adsorption process is considered as the intercalation mechanism for the systems studied in this paper.

They also prolong the polymer molecules to reach the thermodynamic equilibrium significantly. Although the *d*-spacing of the composites shows a similar trend as a function of the residual solvent for different kinds of solvent, the final *d*-spacing of completely dried nanocomposites from different solvents depends on the solvent. While the PS nanocomposite from tetrahydrofuran has

Table 1
Comparison of the parameters of different solvents studied in the PS nanocomposites system

Solvent	Boiling point (°)	Solubility parameter $(\mathrm{cal/cm^3})^{1/2}$	To PS	To amine	*d*-Increment
Toluene	110.6	8.9	−0.6	−0.6	1.4
Ethyl acetate	77	9.1	−0.4	−0.8	1.5
Teterahydrofuran	65	9.1	−0.4	−0.8	1.9
Methyl ethyl ketone	80	9.3	−0.2	−1.0	1.4

Polystyrene 9.5 and hexadecylamine 8.30 PEMA 8.9.

relatively large *d*-spacing increment of 1.9 nm, the sample from ethyl acetate has a *d*-spacing increment of 1.5 nm, and the samples from toluene and methyl ethyl ketone have similar *d*-spacing increment of 1.4 nm. After these samples are annealed at 165 °C for 6.5 h in the vacuum oven, the *d*-spacing of all these samples became identical. This suggests that the difference in the *d*-spacing of PS nanocomposites from different solvents is not caused by the amount of polystyrene intercalated, instead, by the different conformation of polystyrene within the silicate layers. Polystyrene intercalated into the silicate layers with the help of solvent. With the gradual evaporation of solvent, the polystyrene chain conformations depends on the type of solvent, therefore, caused a different *d*-spacing. However, after these samples are annealed at a temperature much higher than the glass transition temperature, the various degree of restriction imposed on the polymer chains by different solvents were eliminated and the polymer chains assumed thermodynamically equilibrium state within the confined environment under the annealing condition. Consequently, the *d*-spacing for all the samples from different solvents achieved the same value.

The assumption about two states of intercalated solvents can be further confirmed by the evaporation temperature of the residual solvent as a function of its concentration as shown in Fig. 6. Independent of the boiling temperature of pure solvent, the evaporation temperature of all the intercalated solvents in this study is very close, around 150–160 °C, when the residual solvent is more than 5 wt%, though it increases gradually as solvent evaporates. The evaporation temperature shows a drastic increase when the solvent concentration is reduced to about 2–4 wt%, which coincides with the value for the *d*-spacing to show the minimum. The large difference in the evaporation temperature reflects the difference of the interaction between solvent molecules and the polymer molecules, i.e. the two different states of solvent molecules.

The situation for solution intercalation of poly(ethyl methacrylate) (PEMA) is little different from polystyrene solution intercalation. Unlike polystyrene that cannot intercalate into the silicate layers from any solvents when the polystyrene concentration is low, whether or not the PEMA intercalates into the silicate layers at low concentration range depends on the type of solvents used. From the solvents like dioxane, methyl ethyl ketone and ethyl acetate, no *d*-spacing change is observed for the completely dried PEMA composites compared to the organoclay. However, for solvents like ethanol, ethyl ether, toluene, and methyl chloride, intercalation is obvious, which is suggested by the *d*-spacing increment. Fig. 7 shows the *d*-spacing increment of the poly(ethyl methacrylate)–clay composites with 10 wt% of PEMA as a function of the solvent solubility parameter [27]. It appears that the intercalation capability of PEMA via solution method is not directly related to the solubility parameter of the solvents. However, if the solubility parameter is separated into three different components: component due to dispersion forces, polar forces, and hydrogen bonding, and plot the figure of *d*-spacing increment as a function of these different components, we can find that the intercalation capability of PEMA strongly relates to the hydrogen bonding component. The shape of this figure is very similar to the result obtained from our group about the solubility parameter relationship between the polymer and swelling agent [26]. Only in the very narrow middle range of solvent hydrogen bonding strength, PEMA cannot intercalate into the silicate galleries at low polymer concentration. Since the solvent plays a role very similar to the swelling agent, it is easy to understand the observation of the same phenomenon for the situation of the solvent and the swelling agent.

Different from polystyrene, poly(ethyl methacrylate) is a polymer that can form strong hydrogen bonding. It is possible that the ability of PEMA to form hydrogen bonding with surfactant molecules makes it easier for PEMA to intercalate into the silicate galleries than for polystyrene. However, similar interaction also exists between the surfactant and solvent molecules and solvent molecules and polymer chain. Therefore, there is a balance between these different interactions and the final intercalation result is the consequence of the combination of these different

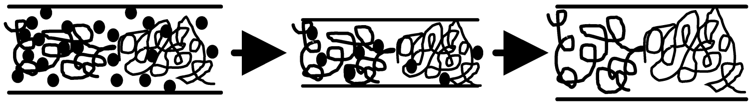

Fig. 5. The schematic representation of the solvent evaporation process.

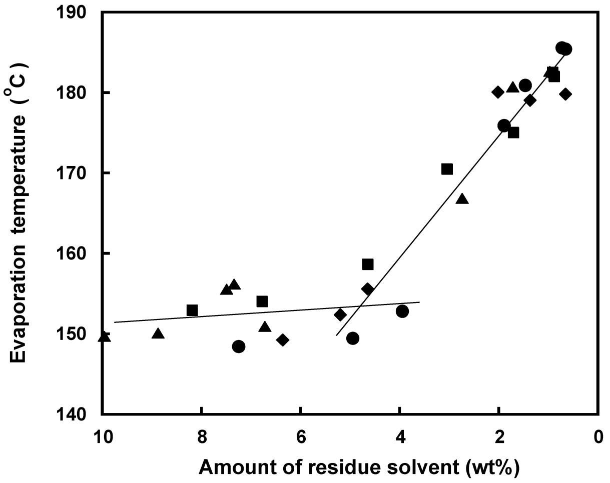

Fig. 6. The evaporation temperature of the solvents (●) methyl ethyl ketone, (▲) THF, (■) toluene, and (◆) ethyl acetate from the polystyrene–clay cast films.

interactions. Although the specific quantitative conclusion could not be drawn at this stage because of the lack of the solubility parameter (including three components) of hexadecylamine and polymer, it is clear that the solution intercalation process is not only controlled by the compatibility between the polymer and surfactant.

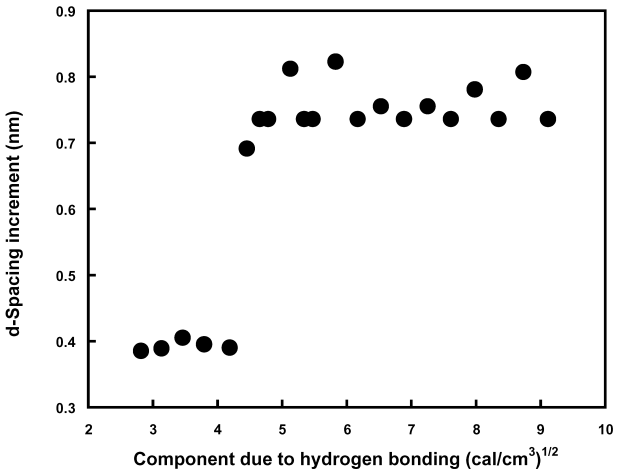

Fig. 8. *d*-Spacing increment of PEMA nanocomposites with 10 wt% of PEMA from the solvent mixture of ethanol and ethyl ether with different volume fraction.

Fig. 8 shows the *d*-spacing increment of the organoclay in a mixed solvent of diethyl ether and ethanol. Assuming that the hydrogen bonding component of a solvent mixture is proportional to the solvent concentration, systematic change of the hydrogen bonding contribution of the same solvent systems on the polymer intercalation can be studied. While this assumption is not always true, it is a reasonable assumption for the systems studied here as the ethanol can

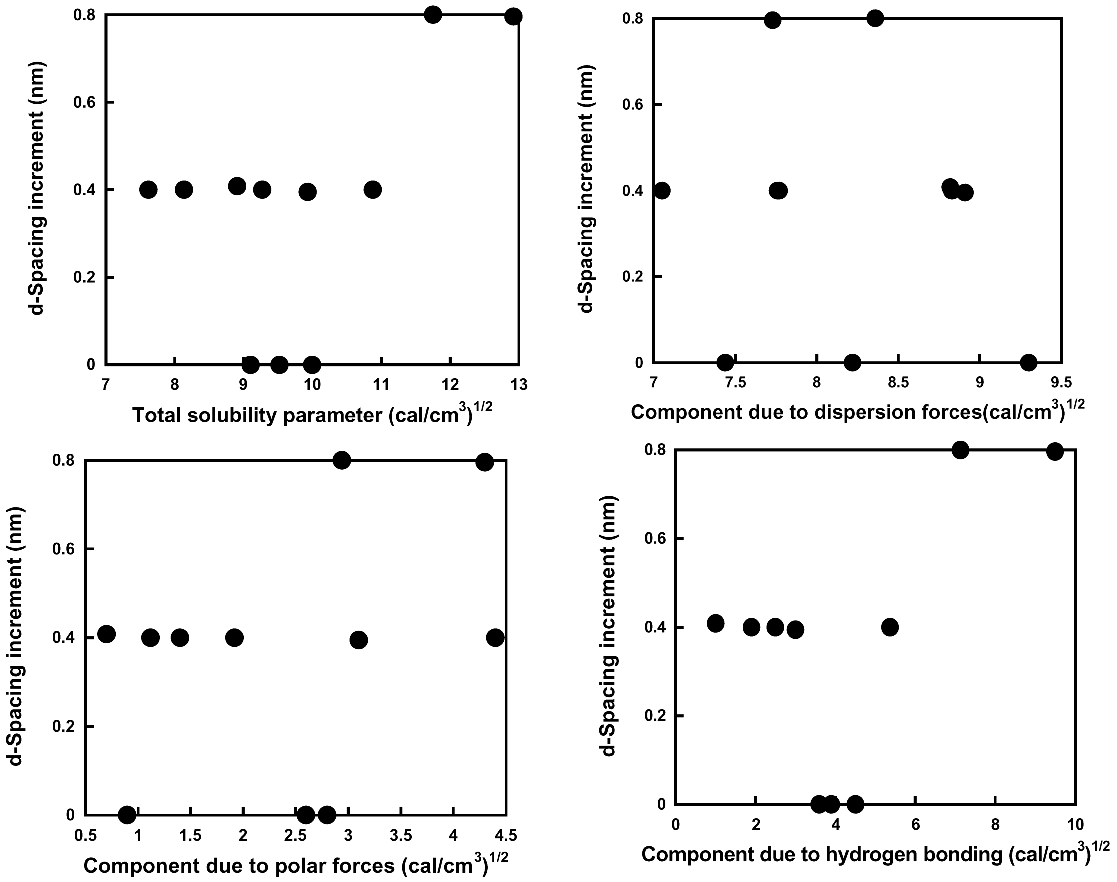

Fig. 7. *d*-Spacing increment of poly(ethyl methacrylate)–clay composite with 10 wt% of PEMA as a function of the solubility parameter of the solvents. Top: a and b; bottom: c and d.

hydrogen bond to ether and have relatively good molecular level interaction. Reflecting the soundness of this assumption, the *d*-spacing of the organoclay suddenly increased when the solubility parameter (hydrogen bonding component) of the solvent mixture is around 4.5 $(\text{cal/cm}^3)^{1/2}$. In Fig. 7(D), the *d*-spacing of the organoclay in the pure solvent systems also increased abruptly around 4.5 $(\text{cal/cm}^3)^{1/2}$. Between 3.0 and 4.5 $(\text{cal/cm}^3)^{1/2}$ in Fig. 8, the *d*-spacing increment is quite small, which is also in good agreement with the result in Fig. 7(D). Unfortunately, even a pure diethyl ether has a solubility parameter (hydrogen bonding contribution) of 2.5 $(\text{cal/cm}^3)^{1/2}$. Therefore, the expected slight increase of *d*-spacing increment observed below this value for pure solvent systems could not be tested for the mixture systems.

4. Conclusion

Polystyrene–clay nanocomposites are prepared via solution intercalation method. There is a critical concentration of polystyrene for the nanocomposites to be successfully prepared by the solution intercalation method. Polystyrene nanocomposites prepared from the solution method shows similar *d*-spacing change as from the melt blending method, which is about 1.2 nm. Comparison between the solution intercalation of poly(ethyl methacrylate) and polystyrene indicates that the competition between polymer–surfactant, surfactant–solvent, and polymer–solvent interaction plays an important role on the polymer intercalation from solution. The study of solvent evaporation process from the polystyrene intercalated silicate galleries shows that there is a minimum *d*-spacing increment of the nanocomposites when solvent concentration is around 2–4 wt%. Solvent concentration below or above this amount all results in the large *d*-spacing increment, which indicates that the solvent molecules within the silicate galleries have two different interaction with the polymer molecules.

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