

The Effects of Experimental Parameters on the Extent of Intercalation of PMMA/MMT Nanocomposites Prepared in Solution

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ABSTRACT: The effects of various parameters on nanocomposite preparation by solution intercalation were studied. Nanocomposites of poly(methyl methacrylate) (PMMA) and commercial organically modified montmorillonites (MMT) were prepared in solvents of different polarities, from strongly polar protic ethanol to nonpolar toluene. The extent of intercalation was studied in correlation with processing parameters, such as time of intercalation, temperature, concentration of PMMA/MMT in solution, and method of preparation determined by X-ray diffractometer.

Solvent polarity was the most important of all studied parameters. In general, the lower the dielectric constant of the solvent, the better the intercalation is; however, the exact correlation also depends on the type of modifier. Another important parameter is isolation of the nanocomposite, whereas other studied parameters are of minor importance. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1182–1187, 2009

Key words: clay; nanocomposites; X-ray; DSC; glass transition

INTRODUCTION

Nanocomposites composed of polymers and montmorillonites (MMTs) often exhibit a remarkable improvement in mechanical properties, heat resistance, barrier properties, decreased flammability, etc. at much smaller filler loads than in classical composites; therefore, they have attracted great interest, both in academia and in industry. Nanocomposites based on various polymers, thermoplastics, as well as thermosets have been prepared by solvent intercalation, melt intercalation, or in situ polymerization.^{1,2} Melt intercalation is the most preferable method because it is compatible with current industrial processes and is usually environmentally friendly. On the other hand, due to the high viscosity of the system, the homogeneous distribution of MMT can sometimes only be achieved on a macroscopic level.

Solution intercalation proceeds in solvents that dissolve the polymer and swell the MMT particles. Due to the large amounts of solvents needed, it is

not a preferred method of preparation. Nevertheless, solution intercalation can find application in fields where thin films are needed, such as coating³ and membrane⁴ applications.

Nanocomposites are usually prepared in such a way that MMT is first swollen in a solvent and then the polymer or polymer solution is added and mixed. The polymer chains intercalate between the MMT layers and displace the solvent. Intercalated nanocomposites are formed upon solvent removal. The method is preferentially used to make water-soluble polymer nanocomposites, such as poly(ethylene oxide)^{5–7} or polyvinyl alcohol.⁸ Solution intercalation has also been used to make various thermoplastic (polystyrene,⁹ styrene-acrylonitrile,¹⁰ polymethyl methacrylate¹¹), thermoset [poly(glycidyl methacrylate-co-methyl methacrylate)],¹² epoxy,¹³ as well as elastomeric polymer/MMT nanocomposites (chlorobutyl,¹⁴ polyisoprene,¹⁵ ethylene propylene diene terpolymer, ethylene vinylacetate¹⁶). Nevertheless, there are still many open questions about the influence of various parameters, such as the type of solvent, type of MMT modifier, temperature, etc., on the extent of intercalation and nanocomposite properties. The literature reports on different results depending on the selected parameters, which leads to nonuniform conclusions. For example, Vaia et al.¹⁷ reported that polystyrene (PS)/MMT nanocomposites cannot be formed in toluene, whereas other authors have obtained the opposite results.¹⁸

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The difference in the obtained results could also be explained by the influence of the MMT modifiers, which were dioctadecyldimethylammonium bromide¹⁷ and hexadecylammonium chloride.¹⁸

The effect of solvent on intercalation has also been known for a long time. The early report on poly(ethylene oxide) (PEO)/Na-MMT nanocomposite preparation in various polar solvents showed that the polarity of the solvent is critical in facilitating the insertion of polymer chains between the silicate layers.¹⁹ The use of chloroform as a solvent for the preparation of a polylactide (PLA)/MMT nanocomposite did not result in intercalation but in formation of a superstructure with MMT tactoids parallel to the film surface, leading to an increased Young's modulus.²⁰ Similar behavior was also observed for polycaprolactone (PCL)/MMT.²¹

Intercalation by in situ polymerization in solvent can also be treated as a kind of solvent intercalation. The intercalated PS/MMT nanocomposites were prepared by in situ polymerization in various solvents, and mixtures of solvents and were isolated by precipitation. It was observed that the extent of intercalation depended on the nature of the solvent used.²² Precipitation was successfully used to isolate acrylonitrile-butadiene-styrene (ABS)/MMT,²³ poly(vinylidene fluoride) (PVDF),²⁴ and polyethylene²⁵ nanocomposites; but no intercalation was found when ethylene-acrylic acid copolymer and MMT were precipitated, although the nanocomposite was easily formed by melt intercalation.²⁶

According to all of these results, interactions such as polymer-MMT modifier, solvent-MMT modifier, and polymer-solvent, are cooperative and play an important role in the solution intercalation of polymers. The exact role of those interactions has still not been evaluated. Therefore, the aim of the present study is to get a better insight into the solution intercalation process by studying the effects of various experimental parameters, especially solvent polarity on intercalation. The nanocomposites poly(methyl methacrylate) (PMMA)/MMT were prepared in seven different solvents ranging from highly polarity solvents, such as ethanol and acetone, to nonpolar solvents, such as toluene. Two types of organically modified MMT, differing in type and quantity of modifier, were used; and the process parameters, such as temperature, time of intercalation, solution concentration, and method of nanocomposite preparation, were varied.

EXPERIMENTAL

PMMA

Oroglas MI-2T (Altuglas International, Arkema Group, France), MFI = 2.8 g/10 min ($\epsilon = 3.2$).

MMT

Nanofil 5, Nanofil 2, Nanofil 8, and Nanofil 9 were kindly donated by Rockwood Clay Additives (Germany). Nanofils 5 and 8 differ in quantity (35 and 45%, respectively) of the modifier distearyldimethyl ammonium chloride ($(C_{16}H_{33})_2(CH_3)_2NCl$). Nanofils 2 and 9 are modified with stearylbenzyl dimethyl ammonium chloride ($C_{16}H_{33}(\Phi-CH_2)(CH_3)_2NCl$) (30 and 35%, respectively).

Solvents

Ethanol (96%; $\epsilon = 27.5$), acetone ($\epsilon = 21.01$), butanone ($\epsilon = 18.56$), 1,2-dichloroethane ($\epsilon = 10.42$), THF ($\epsilon = 7.52$), $CHCl_3$ ($\epsilon = 4.81$), and toluene ($\epsilon = 2.38$).

Nanocomposite preparation

In a round-bottom flask, 5 g PMMA and 0.2 g Nanofil were weighed, and 50 g of solvent was added and mixed with a magnetic stirrer for 3 or 24 h at 50°C or at room temperature. Due to the differences in solubility of PMMA in solvents and the large differences in solvent density, the same mass instead of volume of the solvent was used so that the weight concentrations were the same for all solvents. When ethanol was used, the temperature was raised to 85°C due to the low solubility of PMMA at 50°C. The nanocomposite solution was then poured into a Teflon tray and dried, first in air for 24 h then under a vacuum at 80°C for an additional 24 h. The formed nanocomposites were ground to a powder and dried again under vacuum at 80°C for 24 h. In some cases, nanocomposites were also prepared by precipitation in 200 mL of water or ethanol (from $CHCl_3$).

The glass transition (T_g) was measured using a Pyris 1 differential scanning calorimeter (Perkin Elmer). The samples were heated twice from -10°C to 180°C at a heating rate of 20 K/min and cooling rate of 200 K/min. The results of the second heating scan are presented.

The X-ray diffraction patterns of MMT in nanocomposites were determined by using a PANalytical X'Pert PRO X-ray diffractometer ($\lambda = 1.54 \text{ \AA}$, $2\theta = 1.5^\circ$ - 15° , step 0.33°). The X-ray diffraction patterns of MMT in solvents were taken on a Siemens D-5000 diffractometer using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) in 0.04° steps from 2° to 10° (in 2θ) with 5 s per step.

RESULTS AND DISCUSSION

During nanocomposite preparation, it was observed that the mixtures prepared in low dielectric constant (ldc) solvents were almost transparent, whereas the mixtures prepared in high dielectric constant (hdc) solvents were turbid white. During swelling in ldc

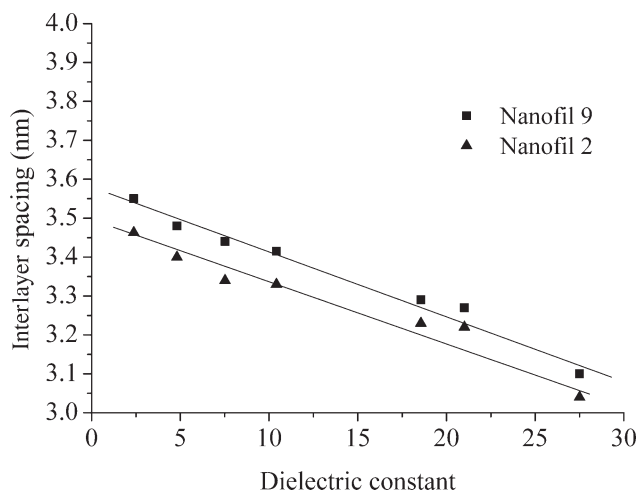


Figure 1 MMT interlayer spacing of Nanofil 2 and Nanofil 9 in a nanocomposite as a function of the dielectric constant of the solvents used.

solvents, Nanofils disaggregate and consequently become transparent to visible light.

The influence of solvent polarity on MMT interlayer spacing (d_{001}) in dry nanocomposite, depending on the type of modifier, is shown in Figures 1 and 2. When Nanofils 2 and 9, with one stearyl chain and benzyl group, were used, the interlayer spacing decreases linearly with increasing dielectric constant (Fig. 1) and can be described with the following equation:

$$d_{001} = d_0 - k \cdot \varepsilon \quad (1)$$

where $d_0 - d_{001}$ is the interlayer spacing obtained in a theoretical solvent with $\varepsilon = 0$; k is the constant, whose value depends on the type and quantity of the modifier.

In the cases of Nanofil 5 and Nanofil 8, modified with two long stearyl chains, the decrease is observed only at a dielectric constant up to 10. Above that value, the results scatter around a constant value of 3.6 nm (Figure 2). According to these results, the modifier with two hydrocarbon chains makes the surface of the MMT layer so hydrophobic that solvation and swelling by polar solvents is prevented.

The influence of solvent on intercalation can be explained by increased solvent-modifier interactions with decreased solvent polarity. Long stearyl chains interact with low dielectric constant (ldc) solvents, but not with high dielectric constant (hdc) solvents. Therefore, the Nanofils strongly swell in ldc solvents while only slight swelling is observed in hdc solvents. The XRD diffractogram of the Nanofil5/toluene mixture shows no peak indicating an exfoliation or at least a strong increase in interlayer spacing (above 5 nm), while in a mixture of Nanofil5/ethanol the peak of Nanofil 5 is observed at 2.48° which corresponds to an interlayer spacing

of 3.5 nm, only slightly lower than in the nanocomposite (3.6 nm). As shown in studies on organically modified montmorillonites, the type of modifier strongly influences the interlayer spacing and swelling in solvents, although no correlation has been found between the two.^{3,27} There was also no clear relationship between the swelling and the surface tension of the solvent or its solubility parameter. Some authors have reported on a correlation between interlayer spacing and swelling, but the results are presented for only one modified MMT and a smaller number of solvents than above.²⁸ We can assume that, the better the swelling, the more room there is for the polymer molecule to intercalate and, therefore, the interlayer spacing increases.

Greater interlayer spacing in nanocomposites prepared with Nanofils 5 and 8 as compared with Nanofils 2 and 9 can be attributed to stronger isotropic dispersive interactions of the solvents (and maybe also of the PMMA) with the MMT modifier having two stearyl chains compared to the one with one stearyl chain.

The interlayer spacing of Nanofils 2 and 9 differ by only 0.13 nm. When nanocomposites were prepared in ethanol and toluene, the interlayer spacing of Nanofil 2 increased by 1.12 and 1.54 nm, respectively. In Nanofil 9, with a higher modifier content and greater interlayer spacing, the increase is slightly smaller, approximately 1.05 and 1.50 nm. Similar results were obtained for other solvents presented in Figure 1. The difference is much bigger than those found in Nanofils 5 and 8. The interlayer spacing of Nanofils 5 and 8 differ by 0.75 nm, whereas the difference in interlayer spacing of all nanocomposites made of Nanofils 5 and 8 is only ≈ 0.1 nm. The increase was therefore much bigger

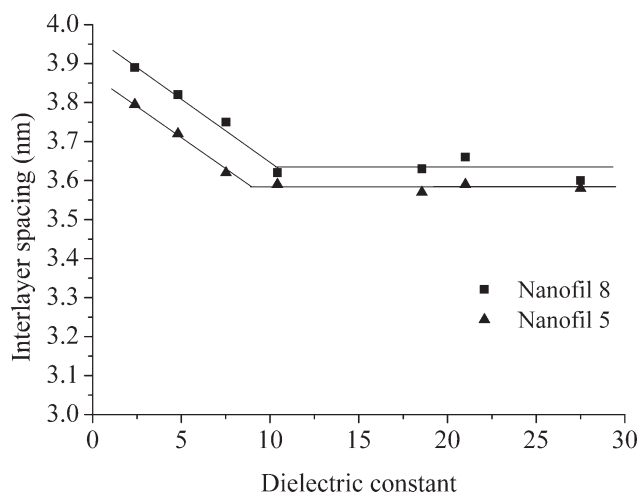


Figure 2 MMT interlayer spacing of Nanofil 5 and Nanofil 8 in a nanocomposite as a function of the dielectric constant of the solvents used.

TABLE I
Increase in Interlayer Spacing in Nanocomposites Prepared in Ethanol and Toluene

	MMT interlayer spacing d_{001} (nm)	Nanocomposite prepared in ethanol d_{001} (nm)	Δd_{001} (nm)	Nanocomposite prepared in toluene d_{001} (nm)	Δd_{001} (nm)
Nanofil 2	1.92	3.04	1.12	3.46	1.54
Nanofil 9	2.05	3.10	1.05	3.55	1.50
Nanofil 5	2.78	3.58	0.80	3.80	1.02
Nanofil 8	3.53	3.60	0.07	3.89	0.36

in Nanofil 5 (0.80 and 1.02 nm) with smaller interlayer spacing than in Nanofil 8 (0.07 and 0.36 nm; Table I).

From this point of view, the intercalation is better if MMT with a low modifier content and smaller interlayer distance is used, which is unlikely. To find an explanation for these results, all the Nanofil were extracted in ethanol for 24 h in a Soxhlet apparatus and analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The diffractograms of extracted Nanofil 5 and 8 were the same with the basal peak at 3.68° . This value corresponds to an interlayer spacing of 2.4 nm, which is much smaller than before the extraction (Table I).

The results of TGA for Nanofil 5 and 8 are shown as example in Figure 3. The weight loss of extracted Nanofil at 1000°C is $\sim 35\%$, whereas the weight loss of original Nanofil 5 and 8 is 39 and 46%, respectively. According to TGA analysis, Nanofil 5 and 8 contain 4 and 10% quaternary ammonium salt in excess, which was removed by extraction. If we compare the interlayer spacing of original Nanofil (Table I) with the results of TGA, we can conclude that 1 wt % excess of distearyldimethyl ammonium chloride adds ≈ 0.1 nm to the interlayer spacing in organically modified MMT.

Similar XRD and TGA results were obtained for Nanofil 2 and 9. The interlayer spacing of both extracted samples was ≈ 1.85 nm. The results of TGA analysis are shown in Table II.

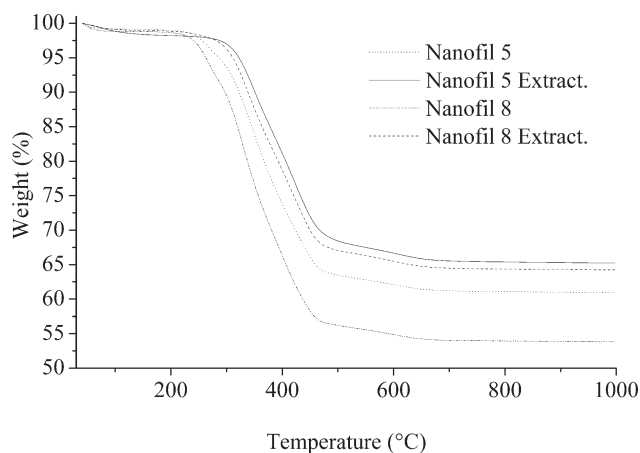


Figure 3 TGA analysis of pristine and extracted MMT.

According to TGA and XRD analysis, different commercial MMTs, modified with the same modifier, do not differ in the quantity of exchanged cations but rather in the excess of modifier salt that is distributed within the MMT layers. Because the interlayer spacing in nanocomposites made of Nanofil 5 and 8 differ by only ≈ 0.1 nm, we can conclude that intercalation depends on interactions of the solvent-polymer-MMT system and not on the interlayer distance of MMT. In our experiment, the influence of excess modifier is small and it can be attributed to strong interactions between the alkyl chain bound to MMT and the alkyl chains of the excess modifier.

All the results presented above were obtained at an intercalation time of 24 h and at 50°C (except ethanol), which might not be practical for application. Therefore, the influence of other parameters that might affect intercalation was investigated.

The influence of time on intercalation is of small importance. The interlayer spacing in the nanocomposite was the same when suspension was mixed for 3 or 24 h, which means that intercalation is a relatively fast process.

A series of nanocomposites were prepared in toluene and chloroform at various temperatures (25 , 50 , and 75°C). XRD analysis showed that the interlayer distance was the same for all nanocomposites. Therefore, increasing the temperature will increase the solubility of the polymer and reduce the time for nanocomposite preparation, but it will not improve the intercalation.

The increased concentration of the PMMA/MMT mixture in toluene (up to four times) also did not result in better intercalation. Actually, this result is expected because the concentration of PMMA/MMT slowly increases during the solvent evaporation up

TABLE II
Weight Loss of Original and Extracted Nanofil During Heating up to 1000°C

Sample	Weight loss (%)	Sample	Weight loss (%)
Nanofil 5	39.1	Nanofil 2	32.9
Nanofil 8	46.2	Nanofil 9	37.2
Nanofil 5, extracted	34.8	Nanofil 2, extracted	28.7
Nanofil 8, extracted	35.8	Nanofil 9, extracted	29.0

to 100%. Therefore, we cannot find any differences even if they exist in the liquid phase.

Ultrasonic mixing is very often used for the preparation of nanocomposites.²⁹ It was reported that ultrasound increases the interlayer spacing of clay particles in PEO/MMT nanocomposites.³⁰ A comparison of diffractograms of nanocomposites prepared by sonication and stirring is shown in Figure 4. In our experiments, we have mostly observed a narrowing of the basal signal in the XRD diffractogram and only a negligible shift of the peak toward a lower angle. Because it is not likely that the broader peak in a stirred sample is a consequence of partial exfoliation, we believe that the stacking order of the silicate layers is more regular and uniform in the nanocomposite prepared by ultrasound.

Because precipitation from solution is a frequently used method of nanocomposite separation and due to the observed influence of the solvent on the intercalation of PMMA between the layers of MMT, we prepared a series of experiments in which the nanocomposites were precipitated as described in the Experimental section. The influence on PMMA/Nanofil 5 nanocomposites is shown in Figure 5 as an example. Reduction of interlayer spacing is observed in all precipitated samples compared with dried ones. Some scattering of results is observed, which can be attributed to variations in experimental conditions during the precipitation, such as the rate of nonsolvent addition or mixing. According to our knowledge, only one article has discussed the difference between drying and precipitation on interlayer spacing.²⁴ During the preparation of PVDF/MMT nanocomposites from DMF solution, it was observed that exfoliated nanocomposites were formed during precipitation, whereas only phase-separated or inter-

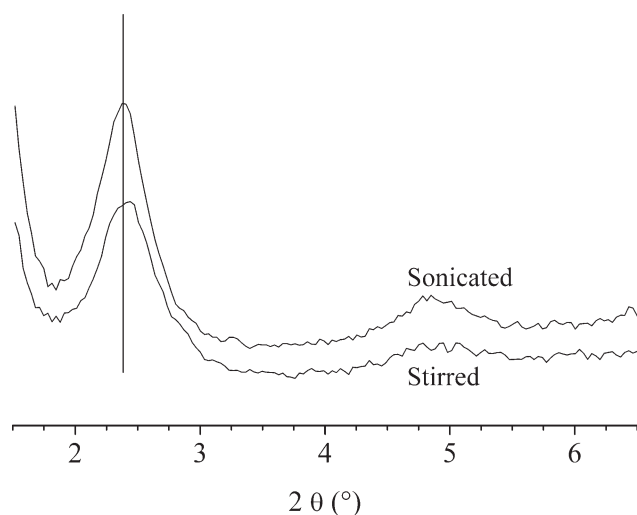


Figure 4 X-ray diffractograms of PMMA/Nanofil 5 nanocomposites prepared in 1,2-DCE, mixed by ultrasound or magnetic mixer.

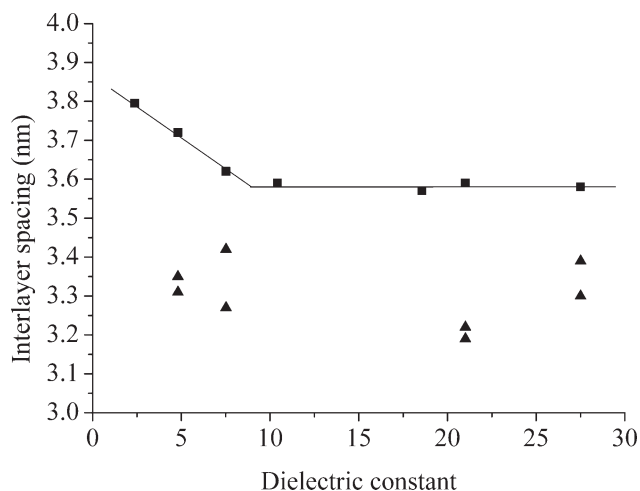


Figure 5 MMT interlayer spacing of PMMA/MMT nanocomposites as a function of dielectric solvent prepared by precipitation (Δ) and drying (\blacksquare).

calated nanocomposites were formed on drying (depending on the type of modifier). It appears that fast kinetics during the precipitation froze a metastable exfoliated morphology, whereas the slower kinetics of the evaporating solvent from the solution cast films permitted a more equilibrated intercalated or phase-separated structure. In our experiments, the results are opposite. Due to favorable PMMA/MMT interactions, the intercalation is better during the slow evaporation of the solvent. During the addition of a nonsolvent, part of the PMMA molecules seems to coagulate and drop out of the MMT layers. The smaller part of PMMA molecules that stay between the MMT layers precipitates as a nanocomposite. This was confirmed by slow cooling (in air) of the PMMA/MMT mixture in ethanol. PMMA is only soluble in ethanol above 50°C, so it starts to precipitate on cooling, whereas MMT is still slightly swelled by ethanol. After cooling to room temperature, the precipitate was filtered and XRD diffractograms were taken. The interlayer spacing of slowly precipitated nanocomposites was 3.15 nm. When the sample was heated to 150°C for 2 h, the interlayer spacing increased from 3.15 to 3.48 nm. The result shows that precipitated nanocomposites are not in an equilibrium state and that the intercalation could improve during nanocomposite processing, such as extrusion or injection molding.

Glass transition temperature

T_g of PMMA/MMT nanocomposites have frequently been measured, and the results vary considerably. Some authors observed the increase,^{31,32} whereas others observed a decrease of T_g .^{33,34} In the latter reference, initial sharp decrease is followed by increase of T_g by increasing content of MMT; but even at

10% of MMT, the T_g was still lower than that of pure PMMA.

In our experiments, the T_g of nanocomposites were 111–116°C, which is similar to the T_g of pure PMMA (113°C). The differences are small, and no correlation with interlayer spacing can be found. However, the lowest values were mostly observed in nanocomposites with Nanofils 8 and 9, which contain a high percentage of excess of modifier that seems to act as plasticizer of PMMA.

CONCLUSIONS

We studied the intercalation of nanocomposites prepared from PMMA and four different organically modified MMT in solution as a function of solvents and various processing conditions, such as time, temperature, concentration, mixing, and nanocomposite isolation. Intercalated nanocomposites were obtained in all solvents, which was confirmed by XRD. The dielectric constant of the solvent and the type of modifier have the biggest influence on intercalation. Generally, the lower the dielectric constant of the solvent, the better the intercalation is and the greater the interlayer spacing obtained. The influence of the solvent is not straightforward and depends on the type of modifier. When a modifier with one long alkyl chain is used, the interlayer spacing decreases linearly with increasing dielectric constant. When a modifier with two long alkyl chains is used, the linear dependence is observed only in solvents with a low dielectric constant (up to 10), whereas above that value, the interlayer spacing did not change significantly.

The method of nanocomposite isolation also appeared to have a great influence on intercalation. The interlayer spacing in nanocomposites isolated by precipitation was much smaller than in nanocomposites prepared by solvent evaporation.

The other process parameters, such as the time and temperature of intercalation, concentration and the method of mixing, seem to be of minor importance.

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