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Modification of Clay Crystal Structure with Different Alcohols

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Abstract

Clays attract attention as a nano size material to reinforce the polymers and resins. In this study, montmorillonite clay was modified using industrial solvents that are used in the paint industry. It was shown that the water contact angle could be varied from 20˚ to 140˚ which is a real influence for the clay mineral. X-ray diffraction analysis shows that planar basal space could be altered significantly from 12.57 to 15.40 nm showing 22.5% increase in the interlayer spacing and that is really critical for many polymers and coating applications. This study will highlight many new clay nanocomposites and the formation of various clay nanocomposites.

Keywords

Clay, Solvent, X-Ray Diffraction, Water Contact Angle

1. Introduction

Nanomaterials and nanotechnology have a big potential for many applications. Although there are many regulations regarding the nanomaterials for health issues, still there is a great investment in nanomaterials that can have commercial value. In the area of nanomaterials, nanoclays attracted great attention, as they are abundant in nature and readily available [1] [2] [3] [4] [5]. Moreover, Turkey has a great potential having good resources of clays [1].

Among many types of clays, montmorillonite (MMT) from the smectite family with a planar crystal structure has been the predominantly used clay for polymer reinforcement with intercalated and exfoliated structure in the polymer matrices [2]. MMT clays have been used for many different polymer systems but still not many commercial products have been obtained [2].

In this study, natural clay MMT was modified with different solvents that are used commercially in the coating industry. This is highly important to understand the interaction of the clay and the solvents to be able to use in the paint and coating industry. In this study, MMT was mixed with 6 different industrial solvents for various durations to understand the exfoliation behavior of the clay mineral. The water contact angle studies were also in depth study to understand the repellency and hydrophilicty/hydrophobicity of the clay after certain modifications.

This study demonstrates the importance of the solvents used to modify the clay microstructure opening many new dimensions for the clay research and clay based nanocomposites.

2. Experimental

2.1. Materials and Methods

2.1.1. Materials

Water based dye and 7 different kinds of alcohol (Etyldiglycol, Butylglycol, Dowanol, Isopropyl, Etylalcohol, Butyldiglycol, Isobutanol) were acquired from Dyo Paint Manufacturing and Trading Company Inc., Izmir, Turkey.

2.1.2. Methods

The nanoclay blend was formulated by adding the required weight of nanoclay to different types of alcohol at room temperature to obtain 10% w/w blend and each blend was mixed at 300 rpm by using multi-position digital stirring hotplates at room temperature. Mixing of blend was carried out at 60 and 180 minutes for each types of alcohol to achieve a homogeneous dispersion.

The final blends were poured into Petri dishes and left to stand overnight in an oven at 80˚C. After evaporation of the alcohols, the thin films were peeled off from Petri dishes and samples were characterization by using XRD (X-ray diffraction) and contact angle analysis. The X-ray diffraction analysis was carried out with Bruker D2 Phaser, X-ray diffract meter system with Ni filtered CuK_{α} radiation (λ = 1.54 Å) generated at 45 kV and 40 mA. The diffracted X-ray beam was collected by scanning the detector between 2θ = 1˚ and 80˚. The step size was 0.02˚. Contact angle measurements were taken using a ThetaLite101, Biolin Scientific at ambient temperature. A liquid droplet of 3 μL was deposited in to each sample surface using a testing syringe. The image of contact angle was obtained by a high-resolution digital camera and the contact angle results were based on 3 repeats.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis (XRD)

The XRD patterns of the samples are shown in Figure 1. As shown in Figure X clearly indicates that the strong peak corresponding to the 001 montmorillonite mineral in the 2θ position is approximately 7 degree while, the interlayer spacing

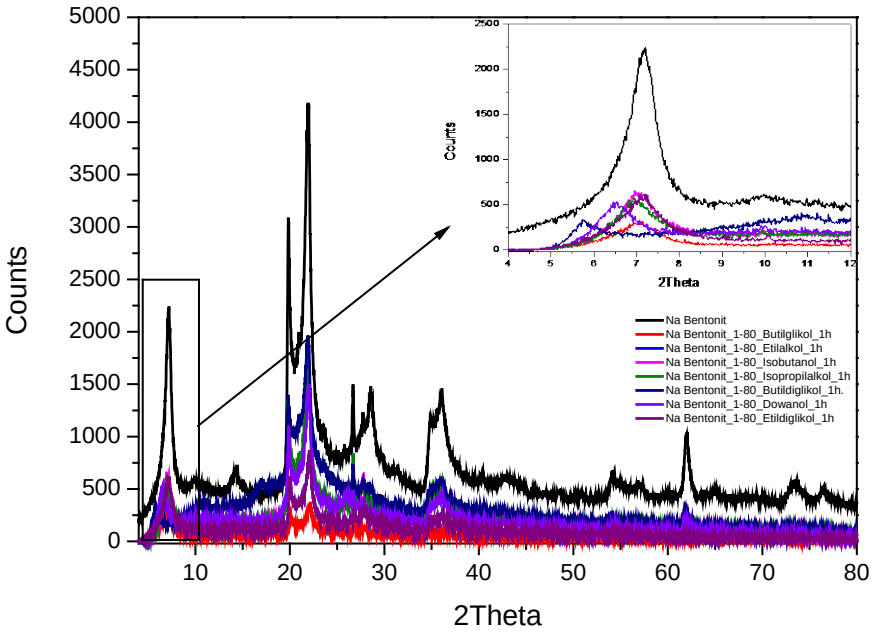

Figure 1. XRD patterns of samples of 1 hours mixing.

in the unmodified clay is approximately 12.41 Å. The other peaks are impurities corresponding to quartz and feldspar [6]. Mixing with different solvents leads to important mineralogical changes which can be seen from XRD patterns of samples (**Figure 1** for 1 hr mixing and **Figure 2** for 3 h mixing). The most noticeable modification takes place in the montmorillonite d (001) peak which shows a reduction in intensity as a result of mixing with various solvents. But, when comparing the results of 1 h and 3 h of mixing, significant differences were not observed between the intensity values.

As shown in **Figure 1**, during the mixing process, the organic compounds are placed between the clay layers, which results in the interlayer spacing increasing. The d (001) montmorillonite mineral peak displacements at 2θ is an appropriate criterion to evaluate the interlayer spacing. Specifically, a decrease in the 2θ angle indicates an increase in interlayer spacing [7]. The interlayer spacing values of the samples which were shown in **Table 1**, were obtained from XRD patterns.

As it can be understood from **Table 1**, interlayer spacing values was increased with the addition of all solvents both 1 h and 3 h mixing process. The maximum shifting value for interlayer spacing values of Na Bentonite was obtained by the addition of butyl diglycol 1h and ethyl diglycol 3 h. This increase may be a sign that the clay layers are separated and distributed more homogeneously in solution.

3.2. Water Contact Angle Results

Figure 3 indicates that the effect of clay-alcohol solution on the water contact, angle changed with mixing time. The contact angle results for the bottom and top surface are measured depending on different types of alcohol. The hydro-

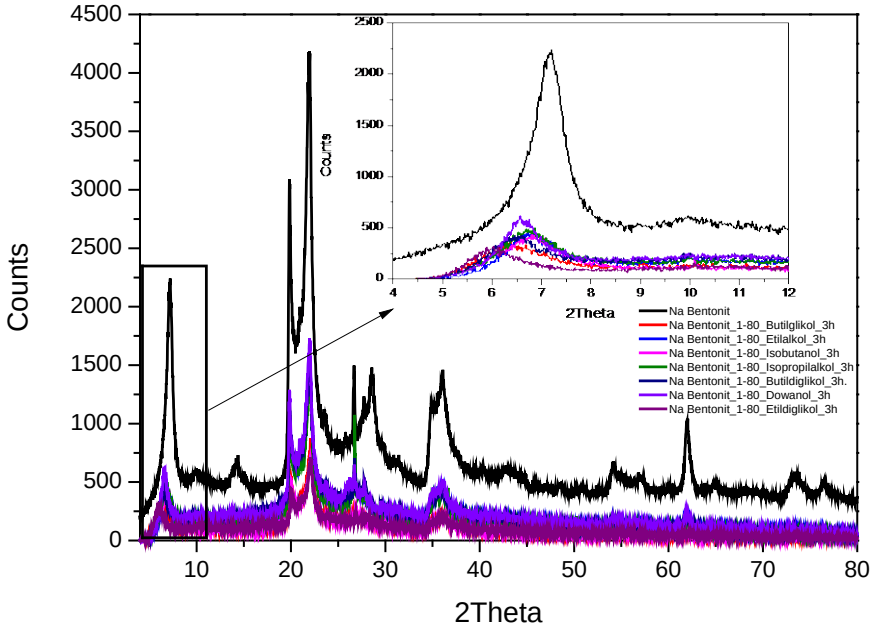

Figure 2. XRD patterns of samples of 3 hours mixing.

Table 1. Interlayer spacing values of the samples.

Samples	Interlayer Spacing Values (Å)	
	1 h Mixing	3 h Mixing
Na Bentonite-Butyl glycol	12.57	13.93
Na Bentonite-ethyl alcohol	12.67	13.16
Na Bentonite-Isobutanol	12.62	13.05
Na Bentonite-Isopropyl alcohol	12.78	13.22
Na Bentonite-Butyl diglycol	15.40	13.68
Na Bentonite-Dowanol	13.44	13.56
Na Bentonite-Ethyl diglycol	12.46	14.73

philic nature of bentonite is attached to its polar interaction between bentonite and solvent [8] [9]. At the same time, when solution concentration is decreased, the water contact angle is decreased [10]. According to results of contact angle, with increasing molecular weight, the contact angle is based on the mixing time of solution.

The initial contact angles without mixing are seen for all samples and their behavior are still hydrophilic like bentonite. Also, the hydrophilicity is increased by increasing mixing time if larger molecular weight alcohols are used for preparing solutions. **Figure 4** shows that the use of alcohol such as dowanol or ethyl diglycol decreased the contact angle and their behavior can be described super hydrophilic. On the contrary, the use of smaller alcohol like isopropyl alcohol tends to be hydrophobic behavior especially for 1 h mixing of solution.

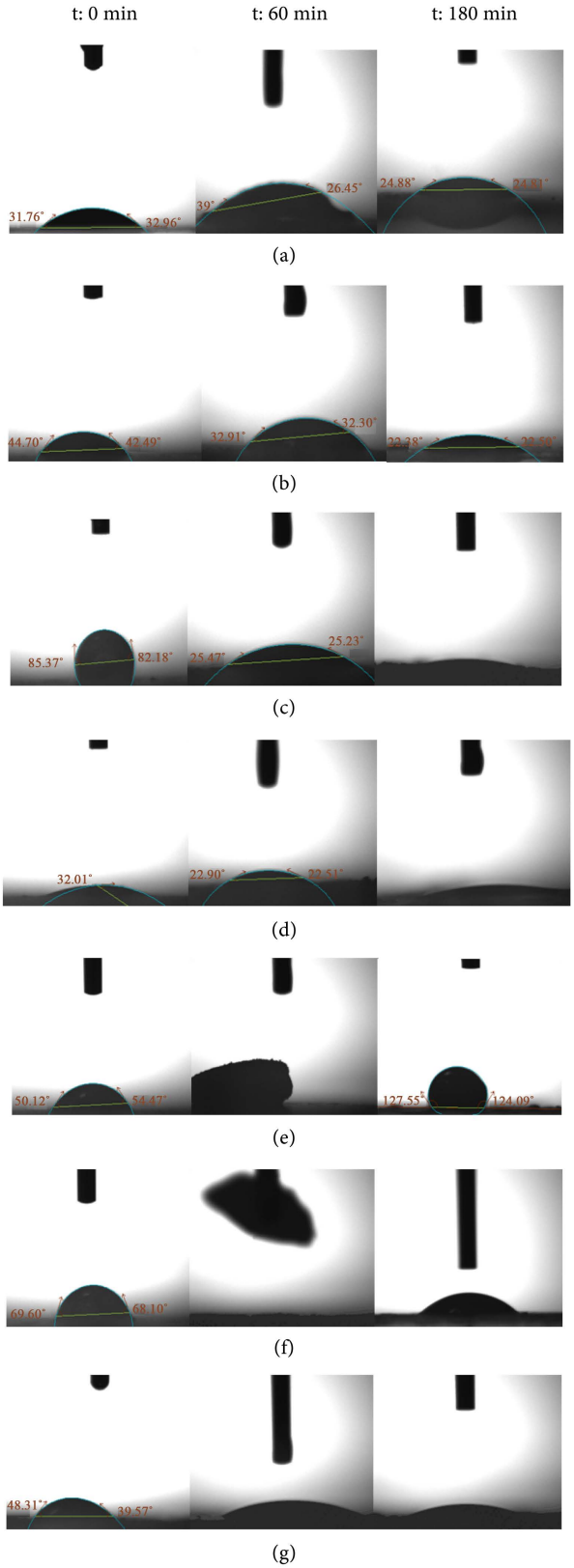

Figure 3. Images of the water contact angle of the (a) Ethyl alcohol; (b) Butyl glycol; (c) Ethyl diglycol; (d) Butyl diglycol; (e) Isobutanol; (f) Isopropyl; and (g) Dowanol polymeric surfaces at different mixing time: 0 min, 60 min and 180 min.

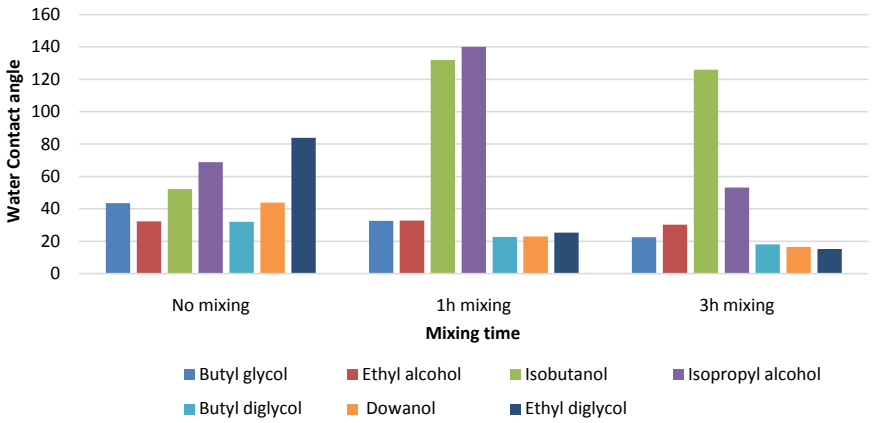

Figure 4. The water contact angles for Ethyl alcohol, Butyl glycol, Ethyl diglycol, Butyl diglycol, Isobutanol, Isopropyl, and Dowanol polymeric surfaces at different mixing time: 0 min, 60 min and 180 min.

4. Conclusion

In this study, a detailed analysis of clays was done to understand the clay behavior with different solvents. It was shown that the clay material could be well exfoliated using suitable solvent for certain time. It is observed that water repellency of the clays could be well adjusted using different solvents. This study shows evidence to fine tune the clay structure for different applications including hydrophilic and hydrophobic nature.

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