The Preparation of Highly Transparent Layered Double Hydroxides (LDHs)-Poly(Methyl Methacrylate) (PMMA) Nanocomposites Sheets by Batch Cell Polymerization Method

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Abstract. Enhancement polymer properties using various clay nanocomposites has been interesting in polymer technology. Herein, a preparation of transparent layered double hydroxides/poly methylmethacrylate (LDHs/PMMA) nanocomposites sheet was achieved by batch cell polymerization. Nanometre-sized MgAl-LDHs in toluene showed well dispersed suspension and was translucent, indicating delamination of LDHs stacks. To prepare PMMA-LDHs nanocomposites, the delaminated MgAl-LDHs in toluene was mixed with methymethacrylate oligomer in order to form slurry of dispersed LDHs in PMMA pre-polymer. The LDHs/PMMA nanocomposites sheet was subsequently prepared using batch cell polymerization at 60°C for 5 hours in water bath and it was then post curing at 80°C for 30 minutes. The optical properties of MgAl-LDHs/PMMA nanocomposites were strongly depending upon a dispersion behaviour of MgAl-LDHs.

1. Introduction

Transparent plastic is material that exhibits transmission of visible light greater than 80% such as polycarbonate (PC), polystyrene (PS) polyethylene terephthalate (PET) and polymethyl methacrylate (PMMA). Transparent plastics are increasingly used to replace glass as construction material because of the ease of fabrication, light weight, safety and cost effective. In fact, the mechanical properties of PMMA, such as stiffness and strength, are much lower than those of metals. However, its mechanical properties are generally improved by applying reinforcement materials such as clay minerals (i.e. montmorillonite, kaolinite, layered double hydroxides). The clay mineral, especially clay nanoparticles, have been studied as a filler in polymeric matrix to enhance mechanical property while maintaining the transparency of the polymer.

The layered double hydroxides (LDHs) is a synthetic clay material containing inorganic layers (layer domain) and the interlayer anions, having the following chemical formula; [Mz⁺ (OH)2<y>][X<z>]<n>/<a>·mH2O (M⁺, z = 1 or 2; M⁺⁺, y = 3 or 4). Due to its structure, the LDHs are adaptively used for several applications such as catalysts [1,2], waste absorber [3], UV/IR absorbers [4–6], flame retardants[7–10], drugs release [11], and nano-fillers in polymer. A study of LDHs as
filler for polymer is widely reported in literatures [10]. The polymer/LDHs nanocomposites show an improvement of mechanical and thermal properties over pristine polymer. It is known that nanometer size additives do not affect optical property of polymer. LDHs normally are hydrophilic and cannot be dispersed in nonpolar solvents and are not compatible with non-polar polymer. Hydrophobicity of LDHs can be altered by intercalating with long chain anionic surfactants (e.g. dodecyl sulfate (DDS). Anionic surfactant can reduce IR absorption and/or flame retardant properties of LDHs. Thus, the LDHs intercalated with anions such as carbonate and borate was studied as additive in polymer [12].

One of simple method mostly used to prepare LDHs/polymer nanocomposites is melt mixing technique. LDHs powder and polymer is mechanically mixed at high temperatures (e.g. 160–200°C). However, dried LDHs powder generally forms aggregate leading poor dispersion in the polymer matrix. This phenomenon can affect the properties of the polymer. Therefore, in this work, LDHs/PMMA nanocomposites were fabricated by mixing MMA oligomer and carbonate intercalated MgAl-LDHs via simple solvent mixing method.

2. Experimental

2.1 Materials

Methyl methacrylate (MMA) was used in an oligomer form. The Mg/Al layered double hydroxides (MgAl-LDHs) powder was supported by SCG Chemicals Co., Ltd., Thailand. 2,2’-Azobisisobutyronitrile(AIBN), commercial grade was purchased from Otsuka chemical Co.,Ltd. Acetone(CH₃COCH₃), Methanol(CH₃OH), Ethanol(C₂H₅O), Iso-propanol(C₃H₇O), Hexane(C₆H₁₄) and toluene(C₇H₈) analytical grade was purchased from RCI labscan (Thailand).

Glass molds should be glossy and should be inspected for defects such as scratch on the surface before use. The PVC gasket stay between two glass molds that look like a sandwich for control thickness of PMMA sheet by using C-clamps.

2.2 Dispersion of Mg/Al LDHs

10%wt/v of MgAl-LDHs powder was prepared by dispersing the Mg/Al LDHs powder in organic solvent with different polarity for their dispersion. The mixture was continuously stirred until it was seen as stable solution. Care must be in order to keep the amount of solvent to be as low as possible.

2.3 Preparation of LDHs/PMMA nanocomposites sheets

The experimental conditions were as follow. The first stage, composites solution, the (200 ml) MMA-oligomer (MMA syrup) was slowly added into 20 ml of MgAl-LDHs (from step dispersion of Mg/Al LDHs) and the solution was vigorously stirred for 30 min. After that 0.4 g AIBN as initiator was added into mixture and then continuously stirred for 30 min. Vacuum process was acquired in order to eliminate bubbles, produced in composites solution. In the second stage, casting polymerization, the composites solution was injected into glass mold having 4 mm spacer. The mold was put into water bath at 60°C for 5 hrs and post curing at 80°C for 30 min. Finally, the glass mold was slowly cooled down to room temperature and LDHs/PMMA nanocomposites sheet was taken out from mold to obtain 1% wt./v of the LDH (1%LDHs).

2.4 Characterizations

The optical transparency of nanocomposite sheet was observed by UV-Vis spectrophotometer (ISR-2600Plud integrating Sphere Attachment, UV-2600, Shimadza) with transmission mode in range of 200-800 nm.

3. Result and discussion

The behaviour of MgAl-LDHs dispersions are summarised in Table 1. The criterions that used to pick intermediate solvent for preparing LDHs/PMMA nanocomposites sheet are miscibility with MMA oligomer and good dispersibility of MgAl-LDHs. For example, acetone and toluene are good solvent for MMA oligomer and good dispersant for LDHs indicated by thick layer of LDHs. However,
both exhibit different LDHs appearance. The LDHs layer was translucent and pearlescent in toluene, whereas there was opaque in acetone as shown in Figure 1.

### Table 1 Observations on selected MgAl-LDHs dispersions

| Polarity index | Dispersion solvent | Apparent of LDHs | Miscibility with MMA oligomer |
|----------------|--------------------|-----------------|------------------------------|
| 9              | Water              | Opaque          | ✗                            |
| 6.6            | Methanol           | Opaque          | ✗                            |
| 5.4            | Acetone            | Opaque          | ✓                            |
| 5.2            | Ethanol            | Opaque          | ✗                            |
| 4.3            | Iso-propanol       | Opaque          | ✗                            |
| 2.3            | Toluene            | Translucent     | ✓                            |
| 0              | Hexane             | Opaque          | ✗                            |

MgAl-LDHs was dispersed in organic solvents with different polarity. All of them showed either precipitated product or no dispersion. It was found that the LDHs in toluene showed stable dispersion as translucent and pearlescent suspension. This was due to the dispersion of LDHs in toluene exhibited a match in the surface of MgAl-LDHs and the solvent polarity, leading of Tyndall light scattering effect. However, the LDHs in acetone and DI water showed poor dispersion as white solid suspension indicating neither types of dispersion is stable for LDHs loading. Hence, the LDHs dispersion in acetone and DI water could not be transparent phase and be seen like aggregates form. The behaviour for these MgAl-LDHs dispersions affected optical properties of nanocomposites sheets as showed in figure 2. It should be pointed out that the better stability and degree of transparency in MMA oligomers, the better the transparency that could be obtained.

![Figure 1](image1.png)

**Figure 1** illustrates photographs of LDHs nanoparticles in (a) DI water, (b) Acetone and (c) toluene
Figure 2. Appearance of LDHs/PMMA nanocomposites sheets a) neat PMMA, b) 1%LDHs in toluene, c) 1%LDHs in acetone and d) 1%LDHs without solvent

Figure 2 revealed that LDHs/PMMA nanocomposites with toluene as solvent showed no significant difference with neat PMMA when observed with naked eye. They were transparent and clear. However, opaque LDHs/PMMA nanocomposites sheet were observed in case of powder sample (without solvent) and with acetone as solvent. This was due to poor dispersion of LDHs in PMMA matrix. UV-Vis transmission spectra of LDHs/PMMA nanocomposites sheet according to samples in Figure 2 under UV-Visible wavelength were showed as seen in Figure 3.

Figure 3. UV-Vis transmission spectra of the LDHs/PMMA nanocomposites with 1% LDHs contents with and without toluene.
Considering optical property of LDHs/PMMA nanocomposites sheet, transmission of each sample at visible light region was determined. Neat PMMA (without LDHs) offered the highest transmission. It could give 91%T. Although transmission of visible light was slightly decreased in sample prepared with toluene, it was still high as 89%T at 1% LDHs loading. Highly optical clarity of LDHs/PMMA nanocomposites sheet was due to disorderly exfoliated morphology leading the LDHs nanoparticles in PMMA matrix were relatively smaller than wavelength of visible light [13]. However, the LDHs/PMMA nanocomposites sheet prepared without solvent showed dramatic decrease of %T as compared to those with toluene. %T of the LDHs/PMMA nanocomposites sheet without toluene were approximately 79% at 1% LDHs loading. This was due to the LDHs nanoparticles were not exfoliated and tended to highly aggregated in PMMA matrix as shown in figure 2.

4. Conclusion
The LDHs/PMMA nanocomposites with MgAl-LDHs were successfully fabricated by solvent mixing process. LDHs nanocomposites dispersed in toluene slightly affected transparency of PMMA. However, LDHs contents caused the agglomeration of LDHs layers resulting in adverse effects. Consequently, we believe this process has provided great potential as simple and convenient method for fabrication of LDHs/PMMA nanocomposites sheet.

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