Rigid palm oil-based polyurethane foam reinforced with diamine-modified montmorillonite nanoclay

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Abstract: This paper presents work on organically-modified montmorillonite (MMT) nanoclay embedded in rigid palm oil-based polyurethane (PU) foam. MMT was modified with organic surfactant diamino propane (DAP). PU foam was fabricated in closed mold, and the amount of DAP-MMT was varied in each foam formulation. The obtained foam was tested for its microstructure and morphology. Appearance of peaks from infra-red spectra corresponding to N-H, C=O, and C-N confirms the formation of PU networks. Scanning electron microscopy (SEM) revealed fine, closed-cellular structure at low clay loading; increasing DAP-MMT content induced larger cell sizes with blowholes. X-ray diffraction (XRD) indicates fully-exfoliated clays at 1 wt. % and partial-exfoliation at 3 wt. % clay loading, suggesting clumping of clays as DAP-MMT content increased.

1. Introduction

Due to its high surface area-to-volume ratio, nano-reinforcements such as nano carbon fibers (CNFs), nano carbon tubes (CNTs), graphenes, and nanosilicas can impart extreme enhancement in mechanical properties when embedded even with little amount in polymers such as polypropylene (PP), polyurethane (PU), and epoxy resin [1–3], which might be the reason they are widely utilized in industries. Even so, the aforementioned materials are synthetically-manufactured; and as such are not environmental friendly and often cost consuming. Researchers over recent years are therefore searching for a more renewable alternatives; and among the ‘green’ nano-reinforcements are montmorillonite (MMT) nanoclay.

Montmorillonites are smectite clays which are well-known for its high swelling capacity and good adsorption/absorption properties [4]. Often these nanoclays undergo surface modification to increase its compatibility with polymer matrix, due to their difference in polarities. According to Zeng et al [3], ion exchange method is the most common method in clay surface treatment, enabling larger interlayer spacing or d-spacing within the nanoclay. This in return allows the nanoclays to be exfoliated or efficiently dispersed within the polymer matrix. Utilization of numerous surfactants for ion exchange method with MMT have been reported elsewhere [5,6]; in this research, we have chosen diamino propane (DAP) as the organic modifier. DAP is a linear-typed surfactant with two amine groups at each end of it polymer chain.

Among the common polymers embedding organoclays in its system is polyurethane (PU). Exists in many forms – foam, thin film, coating, elastomer, etc. – they are vastly utilized in industries as insulation, in deepwater pipeline, packaging, damper, and even for automotive and aeronautic
applications [7–9]. However, PUs consume petroleum feedstock in its production; and this is not favorable with today’s depleting petroleum supply and sustainability issue. Efforts were made to find PU’s greener counterpart, and it has been proven over the past years that oil from plants such as rapeseed, soybean, castor, and palm oil can be modified and used in production of PU [10–13]. This research will focus on palm oil-based PU foam since palm oils are abundant in South East Asia countries like Malaysia and Indonesia.

Current work will be on rigid, palm oil-based PU foam embedded with DAP–modified MMT. The foam was fabricated in closed mold; and the amount of DAP-MMT was varied in each foam formulation. The obtained foam was then tested for its morphology and microstructure. Current work is a continuity of our previous work, aimed to clarify past made claims and to further understand the effect of organic modifier on nanoclay and its polymeric system.

2. Experimental

2.1 Materials

The materials used in this study are MMT K10 nanoclay; hydrochloric acid, HCl; diamino propane, DAP (Sigma-Aldrich); sodium carbonate Na₂CO₃ (BioBasic Inc.); 4,4’-diphenylmethane diisocyanate, p-MDI (Merck Sdn. Bhd.); polyester palm oil-based polyol, POP (MaskimiPolyol, Malaysia); silicon surfactant Tegostab B8404 (Evonik (M) Sdn. Bhd.); and distilled water.

2.2 Modification of MMT

Pristine MMT K10 was first dispersed in distilled water along with Na₂CO₃ and stirred at 250 rpm for approximately 24 hours. The mixture was then filtered and washed several times prior to dried in vacuum oven at 60 °C for 3 to 4 hours. The obtained dried clay was ground into fine powder and re-immersed in distilled water and stirred at 250 rpm for approximately 24 hours. Later, the mixture was heated to approximately 70 °C, before dropwise addition of HCl and DAP aqueous solution. The stirring continues for another 3 hours at 250 rpm and 70 °C, before the mixture was filtered and the filtrate washed several times. It is then dried in vacuum oven at 60 °C for 3 to 4 hours, and the dried clay was ground into fine powder for next stage.

2.3 Fabrication of PU nanocomposites foam

For this study, POP:p-MDI ratio was set at 1:1. Firstly, POP was mixed with distilled water, silicon surfactant, and DAP-MMT (1 to 4 wt. %), stirred at 200 rpm for about 10 minutes, forming homogenous mixture called ‘premix’. p-MDI was then added to the premix and stirred at 500 rpm for 10 to 15 seconds, before poured into closed aluminium mold. It is then left for foaming and curing for 24 hours at room temperature before being demolded, and prepared for testing.

2.4 Fourier-transform infra-red (FTIR) spectroscopy

Infra-red spectroscopy via attenuated total reflectance (ATR) sampling was carried out using Perkin-Elmer Frontier. The foam was scraped into powder and placed onto the ATR crystal. The tip of the force gauge was adjusted to slightly touch the sample. Analysis was then carried out at wavelength range of 4000 cm⁻¹ to 650 cm⁻¹, resolution of 4.0 cm⁻¹, and 16 total scans.

2.5 X-Ray diffraction (XRD)

XRD was carried with 2θ range of 2 to 10°. The value of d-spacing of the organoclay was determined using Bragg’s equation, as given by Eq. 1:

\[ \lambda = 2d \sin \theta \] (1)

where λ is the X-ray radiation wavelength used (λ=1.54056 Å), d is the interlayer spacing of the MMT nanoclay, and θ is the measured diffraction angle.

2.6 Scanning electron microscopy (SEM)
SEM JEOL JSM 6390-LV was used to study the surface morphology of the foam. Samples of size 5 x 5 x 5 mm$^3$ were prepared and coated with gold. The opening voltage was set at 10 kV.

3. Results and Discussion

The infrared spectra of pristine MMT and modified MMT are presented in Figure 1(a), whereas Figure 1(b) illustrates the infrared spectra of pristine PU, and with added 1 and 3 percent weight (wt. %), respectively. Both infra-red spectra for pristine MMT and DAP-MMT portrays the basic characteristic bands of nanoclays: ~3500 cm$^{-1}$ (OH stretching), 1029 cm$^{-1}$ (Si-O stretching), and 797 cm$^{-1}$ (Al-O bending) [14]. Modifying MMT with DAP, several new peaks were present in the spectrum; the most prominent was at 3463 cm$^{-1}$, denoting successful inclusion of DAP into MMT gallery. Further supporting is presence of bands at 3043 and 2948 cm$^{-1}$, attributed to the absorption band of DAP symmetric and asymmetric C-H, respectively. Other bands include 1561 cm$^{-1}$ (NH$_2$ stretching), 1457 cm$^{-1}$ (CH$_3$ and CH$_2$ asymmetrical stretching), and 1325 cm$^{-1}$ (CH$_3$ and CH$_2$ symmetrical stretching) [15]. As for pristine and nanocomposite foam spectra, presence of peaks at 1712 cm$^{-1}$, 1509 cm$^{-1}$, and 1216 cm$^{-1}$ confirms the formation of PU network as these bands represent the bending vibration C=O, N-H, and C-N, respectively. Band at 3314 cm$^{-1}$ and 2280 cm$^{-1}$ represent the free hydroxyl, –OH and isocyanates, –NCO groups in the system, respectively. Peaks at 2924 cm$^{-1}$ and 2850 cm$^{-1}$ were ascribed to the stretching vibration of C-H asymmetric and symmetric, respectively [13].

Figure 1. Infra-red spectra of (a) pristine and organically modified MMT; and (b) pristine PU foam (X0) and PU foam with 1 and 3 wt. % DAP-MMT (X1 and X3)

Figure 2(a) shows the XRD curves for pristine MMT and DAP-MMT, whereas XRD curves for PU foam with 1 wt. % and 3 wt. % DAP-MMT are shown in Figure 2(b). For the MMT’s curves, it can be obviously seen the shifting of peaks from 8.95° for pristine MMT towards the left side at 8.05° for DAP-MMT. This signifies larger interlayer spacing or d-spacing was achieved as the diffraction angle for pristine MMT corresponded to d-spacing of 9.872 Å, whereas DAP-MMT 10.974 Å; confirming successful inclusion of DAP into MMT gallery [14]. As for XRD curves for nanocomposite foams, no significant peaks can be detected upon addition of 1 wt. % DAP-MMT (sample X1), indicating the clays were fully-exfoliated inside the PU [5,16]. Increasing the content to 3 wt. % (sample X3), however; slightly broad elbow can be detected at 2θ value of 6.16°, corresponding to d-spacing value of 14.34 Å. This finding might suggest that only partial-exfoliation clay dispersion can be achieved at higher values of clay loading, in agreement with past publication [17]. As we discussed in our previous work, we thought that the clays tend to agglomerate at higher clay loadings to justify the drop in mechanical properties; and this finding supports our past claims. Past literatures also reported clay agglomeration at higher clay loading [18,19].
Figure 2. XRD curves of (a) pristine MMT and DAP-MMT; and (b) PU foams with 1 wt. % and 3 wt. % DAP-MMT

The microscopic images of PU foams with 0 wt. %, 1 wt. %, and 3 wt. % DAP-MMT are presented in Figures 3(a) through (c), respectively. All obtained foams are of closed-cell foams. It can be observed that the cell sizes were reduced upon addition of 1 wt. % DAP-MMT into the foam formulation. This is thought due to the exfoliated structure, as obtained in XRD result. As clays can function as bubble nucleation site, efficient dispersion of DAP-MMT inside the PU foam matrix can contribute in preventing coalescence, and producing smaller, fine cell structure [20]. As the content was increased to 3 wt. %, the cell sizes increase again. As we claimed previously, it is thought that clay agglomeration occurred at this point; and clay clumping tends to cause cell coalescence by ‘over-blowing’ carbon dioxide gas CO2 inside the cells, hence increasing their cell diameter [21,22]. This finding supports our past claim in explaining the reduction in mechanical properties of the PU nanocomposite foams at higher DAP-MMT loading.

Figure 3. SEM images of (a) pristine PU foam; (b) PU foam with 1 wt. % DAP-MMT; and (c) PU foam with 3 wt. % DAP-MMT

4. Conclusion

In current work, pristine montmorillonite (MMT) was successfully modified with diamino propane (DAP) and embedded inside rigid, palm oil-based polyurethane (PU) foam to study its effect on the foam’s structure and morphology. From the Fourier-transform infrared (FTIR) spectroscopy, the tethering of DAP into MMT gallery was confirmed via detection of peak at 3463 cm$^{-1}$. Peaks that corresponds to C=O, N-H, and C-N bands also confirmed the formation of PU network. Successful inclusion of DAP into MMT was also confirmed through the peak-shifting X-ray diffraction (XRD) pattern, resulting in expanded interlayer gallery from 9.872 Å to 10.974 Å. XRD results also revealed that fully-exfoliated microstructure was achieved for foams with 1 wt. % DAP-MMT loading, and partial-exfoliation at 3 wt. %. Through scanning electron microscopy (SEM), it was noted the reduction in cell size upon introduction of 1 wt. % DAP-MMT into the system, and increment in cell size at 3 wt. %; which we believe owed to the dispersion of the DAP-MMT into the system. To
conclude, inclusion of organically-modified nanoclay into PU foam system results in change in morphology and microstructure of the foam.

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