

Morphologies and Thermal Properties of Palm-oil Based Rigid Polyurethane/Halloysite Nanocomposite Foams

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A bio-based rigid polyurethane (PU) nanocomposite foam was synthesized by reacting palm kernel oil polyol with 4, 4-polydiphenylmethane diisocyanate (p-MDI) at 1:1 NCO: OH ratio via direct mixing method. Nanofiller halloysite nanotube (HNT) was added at three different loadings i.e. 1 wt%, 3 wt% and 5 wt%. Thermal stabilities and morphologies of nanocomposite were investigated. Fourier Transform Infrared (FTIR) analysis confirmed the formation of polyurethane with detection of wavebands at $1,714\text{ cm}^{-1}$, $1,518\text{ cm}^{-1}$ and $1,209\text{ cm}^{-1}$, corresponding to urethane linkages. Scanning electron microscopy (SEM) images displayed bigger cells sizes and smooth cells surfaces, owing to abilities of HNTs to form two nucleating sites and reduced the interfacial tension between the cells. Results from thermogravimetric analysis (TGA) showed good improvements on the thermal stabilities on the foams. In contrast, the flammabilities of the foams did not show significant changes with the addition of HNTs in the systems.

1. Introduction

Productions of polyurethane (PU) foams are heavily relied on petroleum feedstock for their raw materials. However, with future sustainability of petroleum sources and growing concern on environmental problem; a few significant studies had been conducted to find the alternative materials from bio-renewable plant oils such as palm oil (Badri, 2012) sunflower and rapeseed oils (Kairyte and Vejelis, 2015), soybean (Tan et al., 2011) and castor oil (Ganji et al., 2014). Among these plant oils, this study has utilized palm kernel oil-polyol (PO-p) to be reacted with 4, 4-polydiphenylmethane diisocyanate (p-MDI) to form rigid PU foam. Badri (2012) had reported PO-p based PU foam has low density and low water vapor transmission which is good for handling and construction works. Our work is focused on rigid type PU foam because it has the combination of strength and lightweight, which is suitable to be used in sandwich structures, footwear, construction and insulation (Kumar and Kaur, 2013). Furthermore, the rigidity of PU foam can be easily tailored by changing type and ratio of polyol (OH) and isocyanates (NCO). In this work, the OH:NCO ratio was fixed at 1:1 based on our previous study (Nik Pauzi et al., 2014).

PU foam is known as a combustible material which is easily ignited by a small flame source and burn rapidly, following by the released of smoke and toxic gases (Yang et al., 2015). Therefore, the use of flame retardant in PU foam production is important to reduce combustibility and suppresses the toxic fume and smoke that are released from burning. The halogen-containing flame retardants show very negative effect since they give rise to toxic and dense smoke (Yang et al., 2015). Hence natural type flame retardant such as inorganic nanoclays offer an attractive alternative to that of halogen types flame retardants. The char formation induced by nanoclay during combustion helps to suppress oxygen and prevent the burning process of polymer matrix (Rawtani and Agrawal, 2012). Another natural additive such as montmorillonite (MMT) and multi-walled carbon nanotube (MWCN) were also reported as excellent flame retardant (Bkariis et al., 2008). The addition of these nanoclays can transform the common polymeric system into nanocomposite types.

Nanocomposite polymers have drawn a lot of attention since they exhibit superior properties such as excellent modulus and thermal stabilities which far better than that of pure polymers, microcomposites and the traditional polymeric composites (Kiliaris and Papaspyrides, 2014). Nanoclays or nanofillers are abundantly available which can be easily dispersed in the majority of polymers, have high chemical intercalation abilities

and can be organically modified. Natural layered nanoclays such as montmorillonite, bentonite and halloysite nanotubes (HNTs) are the popular choices of nanofillers in polymeric nanocomposites (Neto et al., 2017). Among them, HNTs have the attractive features since HNTs exist as hollow tubes that provide very high surface area, thus giving excellent interactions between the HNTs and the polymer matrix (Alhuthali and Low, 2013). HNTs unique crystal structures resemble carbon nanotubes (CNTs) in terms of aspect ratio, which have a potential to provide a cheap alternative to that of expensive CNTs (Du et al., 2010). Furthermore, HNTs are also biocompatible compared to CNTs (Prashantha et al., 2012). Interestingly, the incorporations of HNTs in polymer matrices such as PU coating (Yan et al., 2017), thermoplastic PU (Marini et al., 2014), polypropylene (Lecouvet et al., 2013), and nylon 6 (Marney et al., 2008) had improved the mechanical properties of the polymers, as well as reduced their flammabilities. HNT helps in improving the flame retardant of polymers (Lecouvet et al., 2013) and directly influences the flammabilities of the polymer composites (Marney et al., 2008). Smith et al. (2017) reported that the incorporation of halloysite nanotubes into an effective and safe flame retardant multilayer nanocoating for polyurethane foam helps in reducing PU foam flammability. However, all the previous works were applied on the solid state polymeric matrices and not on the cellular systems. Therefore, this study was conducted to utilize HNTs as nanofiller in PO-p based PU foams to investigate their effects on morphologies, thermal stabilities and flammabilities. The foams have potentials to be used in various applications such as insulator and core materials for furniture, cooling and freezing systems, in housebuilding and shipbuilding.

2. Experimental part

2.1 Raw material

Palm kernel oil- based polyol, PO-p (Maskimiol PK317) was obtained from Maskimi Polyol Sdn Bhd. Polymeric diphenylmethane 4,4'- diisocyanate (p-MDI) was purchased from Merck Sdn Bhd and silicone surfactant (Tegostab B8404) was bought from Evonik Industries. HNT was supplied by sigma Aldrich. Distilled water was used as blowing agent.

2.2 Preparation of rigid PU nanocomposite foam

Rigid PU nanocomposites foams were prepared by using a direct mixing method according to the formulation shown in Table 1. PO-p, silicone surfactant and distilled water were charged in a 500 ml glass container and mixed using mechanical stirrer for about 2 min until it formed a homogeneous solution. Then, 1 wt% HNT was added into the mixture and further stirred for another 2 min for complete dispersion. Later, p-MDI was charged into the mixture and stirred for 45 s. The PU mixture was then transferred into a mould (dimension of 100 mm x 200 mm x 30 mm). The foam was left for 24 h at room temperature for curing process.

Table 1: Formulation of PU rigid foam

Material	Quantity
Palm oil-based polyol	50 g
Silicone surfactant	4 pphp ^a
Distilled water	2 pphp ^a
HNT ^b	1 wt% and 5 wt %
P-MDI	50 g

^a part per hundred polyol

^b weight percentage of HNT is based on PO-p and p-MDI

2.3 Foam characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

A Perkin Elmer Frontier 2000 FTIR with attenuated total reflectance (ATR) mode was used to identify the functional groups that presence in the sample. The scanning rate was set in the range of 1,000 cm⁻¹ to 4,000 cm⁻¹ with interferometer of 0.2 cm⁻¹.

2.3.2 Scanning Eletron Microscopy (SEM)

SEM was carried out to study the surface morphology of samples and the distribution of HNT particles across the samples. The samples were sputter-coated with thin layer of platinum. The analysis was conducted using a LEO SUPRA 35VP model.

2.3.3 Thermogravimetry Analysis (TGA)

Thermal and degradation properties of the samples were measured with a Perkin Elmer Thermogravimetry Analyzer (TGA 7). The temperature range was set from room temperature to 600 °C with a heating rate of 10 °C /min under nitrogen atmosphere. The weights of samples were fixed around 8–10 mg.

2.3.4 Limiting Oxygen Index (LOI) Testing

The limiting oxygen index (LOI) test measures the minimum oxygen concentration required to support combustion. Samples with dimension of 100 x 12.5 x 12.5 mm³ were held vertically in glass chamber. The test was repeated under various concentrations of oxygen and nitrogen for burning the sample in 3 min. The average of five replicates from each formulation was taken.

3. Results

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of PU nanocomposite foams were shown in Figure 1. Hydroxyl (OH) groups were detected at 3,323 cm⁻¹ where the peaks became broader as the amount of HNT increased. This probably owing to the OH groups that originally present in HNT which the groups can only be completely removed through a dehydroxylation reaction at high temperature i.e. 600 °C - 850 °C (Yuan et al., 2012). Furthermore, the OH groups were also contributed by triglycerides of PO-p which possess less reactive secondary OH groups (Chuaijuljit et al., 2007), as observed in pure PU foam. The existing peaks at 2,918 cm⁻¹ and 2,854 cm⁻¹ were attributed to C-H asymmetric and C-H symmetric of PO-p. The absence of waveband at 2,270 cm⁻¹ in all samples implied that the isocyanate groups (NCOs) were completely consumed during the reaction with PO-P. The detection of characteristic groups of C=O at 1,714 cm⁻¹, N-H at 1,518 cm⁻¹ and C-N at 1,209 cm⁻¹ confirmed the formation of the urethane linkages -RNHCOO-, as found by another researcher (Nik Pauzi et al., 2014).

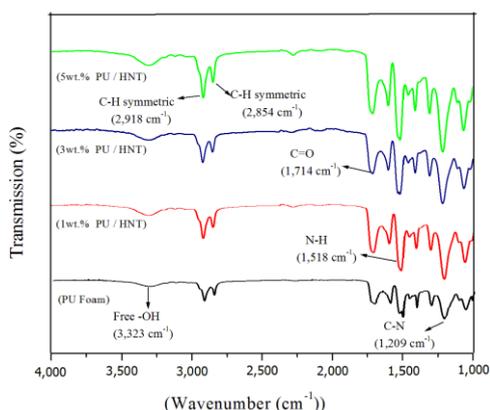


Figure 1: FTIR spectra of PU nanocomposite foams

3.2 Scanning Electron Microscopy (SEM)

Figures 2a-d show the microscopic images of PU foam nanocomposite foams. PU/HNT foams exhibited bigger cell sizes with smooth cell surfaces. Chen et al. (2013) reported that because of the differences in the geometry, the ends and sidewalls of the HNTs act as two distinct nucleating centres or sites, which provide large cell size distribution in final product. PU/HNTs foams showed smoother cell surfaces compared to that of PU foam without HNT, owing to the tubular structure of HNT helps in reducing interfacial tension between PU and HNTs. The extremely fine dimensions, large surface area and rod shape of HNT provide a more intimate contact between the particles, polymer matrix and gas; thus stabilizing the cell wall during foam expansion. These findings are supported by Lorusso et al. (2017) which proposed that Introduction of HNT particles into polymer matrix reduced the energy barrier of bubble formation and growths thus providing better cell formation.

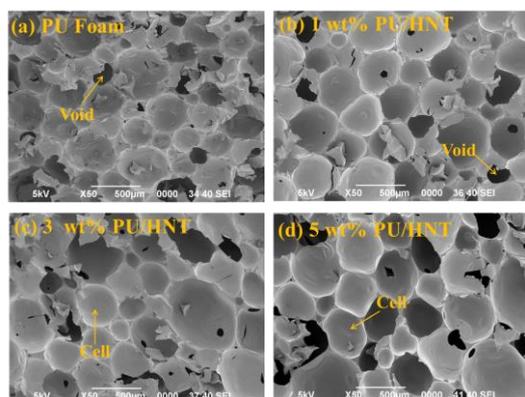


Figure 2: SEM images of PU foams at (a) 0 wt% HNT, (b) 1 wt% HNT, (c) 3 wt% HNT and (d) 5 wt% HNT

3.3 Thermogravimetry Analysis (TGA)

TGA analyses were carried out to study the thermal stability of PU nanocomposite foams. Figure 3 shows the weight losses (TG) and the second derivative of the weight losses (DTG) of PU foams. It is clearly shown that PU nanocomposite foams underwent 3 degradation stages; the first stage occurred at 190 °C, corresponded to the early decomposition of urethane linkages that have low dissociation energies of chemical bonds (Fridrihsone et al., 2013).

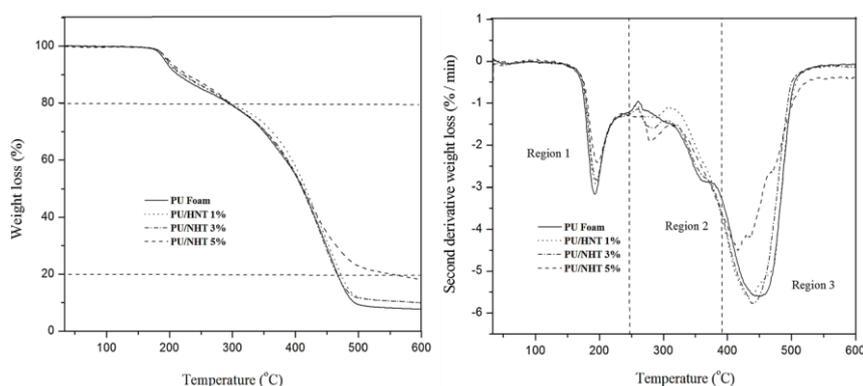


Figure 3: (a) Weight loss (TG) and (b) the second derivative of the weight loss (DTG) of PU/HNT foams

Meanwhile the second decompositions stage occurred at 270 °C– 280 °C representing PU/HNT at 1 wt%, 3 wt% and 5 wt%. The decomposition at this stage was ascribed to the loss of absorbed water on the surface and interlayer of HNTs that rich with aluminol groups (Tham et al., 2014). The third peak of decomposition was occurred at 417 °C – 460 °C, correlated to the decomposition of polyol component (Piszczyk et al., 2014) and dehydroxylation of HNT's interlayer surface (Tham et al., 2014). Thermal stabilities of the foams increased as the percentage of HNTs increased which were summarized in Table 2.

Table 2: Thermal degradation of PU/HNT foams extracted from TG plot

Samples	T ₂₀ % (°C)	T ₈₀ % (°C)	600 (°C) Residual (%)
PU foam	287	466	7.6
PU/HNT 1 %	289	471	9.9
PU/HNT 3 %	291	471	10.0
PU/HNT 5 %	295	551	18.1

It can be seen at 20% weight loss, the degradation temperatures (T₂₀) for all nanocomposite foams (289 °C - 295 °C) were higher than that of pure PU foam (287 °C). The same trend was seen at 80% weight loss (T₈₀) particularly at 5 wt% HNT that showed about 18 % increment in relative with that of pure PU foam. According to Bikiaris et al. (2008), the presence of nanoclay is able to improve the thermal stability of the system because the clay acts as barrier in polymer matrix. The char formation that generated from the oxidation of

HNT provides physical barrier between the polymer medium in retarding the decomposition of polymer. In addition, the large surface area of HNT could restrict the volatilization of decomposed gaseous from bulk polymer onto the gas phase, thus stabilizing the thermoxidation of the polymer. Tham et al. (2014) stated that good interfacial interaction between nanosilica and polymer matrix could increase the degradation's activation energy and leads to a higher thermal stability of polymer composite.

3.4 Limiting Oxygen Index (LOI) testing

Limiting oxygen index (LOI) analysis was carried out to investigate the flammabilities of PU/HNTs nanocomposite foams. A general rule is that if more oxygen is required for combustion, a material will be more difficult to burn, so LOI value will be higher. Figure 4 shows the limiting oxygen index of PU/HNT foams. It can be seen that the effect of HNTs in suppressing the burning process was not that significant although study showed that HNTs can help the formation of protective char layer on the surface of PU-flame retardant compound (Liu et al., 2014). In most cases, the effectiveness of HNTs as flame retardant are applied on many solid state polymers (Yan et al., 2017). However, this study showed that HNTs were not that efficient flame retardant when used in cellular or porous matrices. It was thought that the presence of voids and the mixture of opened/closed cells had formed discrete cells arrangement. The discrete cells prevented the formation of continuous protective char layers on the foam surface, thus poorly retarding the burning process.

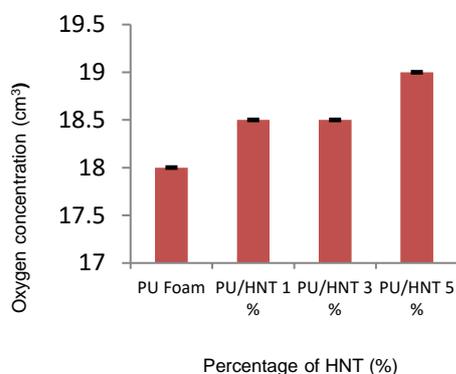


Figure 4: Limiting oxygen index of PU/HNT foams

4. Conclusions

Rigid PU/HNT nanocomposite foams have been successfully prepared by reacting PO-p and p-MDI at 1 wt%, 3 wt% and 5 wt% HNTs loadings via direct mixing method. FTIR analysis confirmed the successfully prepared of PU foams by detection of wavebands that corresponded to urethane linkages. SEM revealed that HNT inclusion provided smooth cell surfaces with bigger cells sizes, due to abilities of HNTs to provide two nucleating sites and reduce the interfacial tension between the cells. TGA and LOI results showed good improvement in thermal stabilities but not effectively significant to suppress the burning process.

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