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Loading Effect of Aluminum Hydroxide onto the Mechanical, Thermal Conductivity, Acoustical and Burning Properties of the Palm-based Polyurethane Composites

(Kesan Penambahan Aluminum Hidroksida ke atas Sifat Mekanik, Kekonduksian Terma, Akustik dan Kebakaran Komposit Poliuretana Sawit)

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ABSTRACT

Effects of aluminium hydroxide (ATH) addition on the properties of palm-based polyurethane composites were investigated. The hybrid composites were prepared by mixing 10 wt% of oil palm empty fruit bunch fiber (EFB) with ATH at varying amount of 2, 4 and 6 wt% of the overall mass of the resin. The compression stress and modulus gave the highest values of 575 and 2301 kPa, respectively at 2 wt% loading of ATH. The compression stress and modulus decreased drastically at 4 wt% (431 kPa and 1659 kPa, respectively) and further decreased at 6 wt% ATH (339 and 1468 kPa, respectively). However, the burning rate is inversely proportional to the loading percentage where the highest burning rate was observed at 2 wt% ATH. Sound absorption analysis indicated a large absorption coefficient at high frequency (4000 Hz) for all samples. The highest absorption coefficient was obtained from PU-EFB/ATH with 4 wt% ATH.

Keywords: Acoustic property; aluminum hydroxide; burning property; mechanical property; polyurethane composites

ABSTRAK

Kesan penambahan aluminium hidroksida (ATH) terhadap sifat komposit hibrid poliuretana (PU) berasaskan sawit telah dikaji. Komposit hibrid PU disediakan dengan menambahkan 10% mengikut berat serabut tandan kosong kelapa sawit (EFB) diikuti dengan penambahan ATH pada peratus penambahan divariasikan pada 2, 4 dan 6% mengikut berat keseluruhan resin. Tegasan dan modulus mampatan adalah pada nilai tertinggi pada penambahan 2% ATH iaitu masing-masing 338 kPa dan 2209 kPa. Pada 4% ATH, tegasan dan modulus mampatan menurun kepada masing-masing 431 dan 1659 kPa dan semakin menurun dengan penambahan 6% ATH kepada masing-masing 379 dan 1468 kPa. Walau bagaimanapun, kadar kebakaran adalah berkadar songsang dengan peratus pengisian dengan kadar pembakaran tertinggi berlaku pada 2%bt ATH. Analisis serapan bunyi menunjukkan pekali serapan yang tinggi pada frekuensi tinggi (4000 Hz) untuk semua sampel dengan PU-EFB/ATH (4% ATH) menunjukkan pekali serapan tertinggi.

Kata kunci: Aluminum hidroksida; komposit poliuretana; sifat akustik; sifat kebolehbakaran; sifat mekanik

INTRODUCTION

Bio-based polyurethane composites have been widely used nowadays. Polyurethane (PU) industry at present is excessively utilizing polyols from petrochemicals as raw materials. Due to a high rate of depletion of petroleum (Carme Coll Ferrer et al. 2008), and requirements for high technology processing system (Badri et al. 2004), vegetable oil such as castor oil, palm oil, soy oil and canola oil has been used to replace petroleum-based polyurethane polyols (Aranguren et al. 2007; Badri et al. 2000; Carme Coll Ferrer et al. 2008; Haq et al. 2008; Husic et al. 2005; Javni et al. 2000; Tanaka et al. 2008).

Addition of natural fibers as reinforcing fillers in polymeric materials has been widely used because of their properties which is environmental-friendly and economics. These lignocellulosic fibers offers low cost, low density, low abrasion and enhanced energy recovery (Khairul Anuar Mat Amin & Khairiah Haji Badri 2007) as well as enhancing the mechanical strength of the bio-composites formed (Badri et al. 2004; Badri et al. 2005; Rozman et al. 2003).

However, natural fiber is an organic material that can easily catch fire. Even though the addition of EFB in the PU system enhanced its mechanical properties, it will also weaken the thermal properties. EFB can also decrease the fire-resistivity due to its property that is easily ignited. In order to increase not only the mechanical property but also the thermal property of palm-based PU, fire retardant namely, aluminum hydroxide (ATH) is added besides EFB.

ATH is unique among other low cost fillers due to its high proposition (34.6%) of chemically combined water with the chemical structure of $Al(OH)_3$. The combined water which is also known as "water of hydration" is stable and unreactive within the processing temperature of many plastics (Bonsignore 1981). Besides low cost, ATH is also odorless, easy to handle, non-toxic, chemically inert and non-volatile (Bonsignore 1981; Wu et al. 2004). When composites filled with ATH is being heated and subsequently burned, the ATH can absorbed the heat which is being applied to it. The absorbed heat is dispersed uniformly in the ATH particles and reduced the heating rate of the composites. The decomposition of ATH will form alumina and water vapor as equation (1):

$$2\,Al(OH)_3 \xrightarrow[\Delta]{} 3H_2O + Al_2O_3. \qquad (1)$$

The water vapor released from the decomposition will dilute any combustible gases involved (Almeida Pinto et al. 2000; Wu et al. 2004). Besides water, the presence of alumina or aluminum oxide (Al_2O_3) as a protective layer on the polymer surface prevents the polymer from being in contact with O_2. Due to the ability to dilute combustible gaseous and slow down fire, ATH has been used as a fire retardant.

Malaysia is one of the biggest palm oil producer in the world. Empty fruit bunch fiber (EFB) is one of the biomass from the palm oil plantation. This agricultural residue can be utilized in natural fiber-based composites. In this paper, the studies on the effect of ATH on the mechanical properties, fire resistivity and the acoustic properties of PU hybrid composites have been carried out. The PU was prepared by reacting the palm kernel oil-based (PKO) monoester (polyol) with 2,4-diphenylmethane diisocyanate and loaded with a fixed amount of EFB at 10 wt%. The amount of the ATH was varied at 2, 4 and 6 wt%.

MATERIALS AND METHODS

MATERIALS

The RBD PKO-based polyol was prepared using method described by Badri et al. (2001). The 2,4-diphenylmethane diisocyanate (MDI) was obtained from Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia. Additives for the polymerization of the polyurethane were glycerol as a chain extender (BHD Laboratory Supplies, England), silicon surfactant (Niax L5440) (Witco Ltd, Singapore) and also tetramethyl hexanediamine (TMHDA) and pentamethyl diethylenetriamine (PMDETA) as catalysts which were also obtained from Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia. Oil palm empty fruit bunch fiber (EFB) was obtained from Malaysian Palm Oil Board (MPOB), Bangi Lama, Malaysia. Aluminum hydroxide (ATH) was obtained from Fluka, Switzerland. The PU system was developed using water as the blowing agent to replace chlorofluorocarbon, CFC.

METHODS

The hybrid composites were prepared using the formulation given in Table 1. The PKO-based polyol, the PU additives and water were mixed using an overhead stirrer with a speed of 1000 rpm to form the resin. EFB and ATH were added based on weight percentage of the overall weight of the resin. The EFB was added at a fixed amount (10 wt%) while ATH was varied at 2, 4 and 6 wt%. The mixture was then reacted with MDI at a ratio of 100:115 (resin to MDI), stirred at 1000 rpm for 10 s. The mixture was then poured into the mould, covered and allowed to cure for 10 min. It was then demoulded after 10 min. The composites were conditioned at room temperature for 16 h before further characterizations.

CHARACTERIZATION

Compression Test The compression test was conducted according to BS 4370: Part 1: 1988: Method 3 standard. Samples were cut to a dimension of 50 mm × 50 mm ×50 mm (length × width × thickness). The test was carried out using Instron Universal Testing Machine model 5566 at a cross-head speed of 50 mm/min until the thickness reduced to 90% of its original thickness. The compressive stress and modulus were recorded as average of five specimens.

Burning Test The burning test was carried out to determine the fire resistivity of the PU hybrid composites according to the ASTM D 5048-90 Procedure B method. The hybrids composites produced were cut to test samples with dimensions of 125 mm × 30 mm × 10 mm (length × width

TABLE 1. Formulation for the preparation of the unfilled PU and PU hybrid composites

Ingredients	0 %	10 wt% EFB		
		2 wt% ATH	4 wt% ATH	6 wt% ATH
PKO-based polyol	90	90	90	90
Glycerol	10	10	10	10
Niax L5440	3	3	3	3
TMHDA	0.46	0.46	0.46	0.46
PMDETA	0.49	0.49	0.49	0.49
Water	4.00	4.25	4.30	4.35
Total pbw	107.95	108.20	108.25	108.30
EFB	-	10.82	10.82	10.83
ATH	-	2.16	4.33	6.50
Ratio of resin:MDI	100:115	100:115	100:115	100:115

× thickness). The test samples were then clamped at one end so that its position is at 30°. The blue flame from the Bunsen burner was positioned within the range of 25 – 30 mm from the specimens for 5 s. The overall burning time and the final length of the specimens were recorded. The burning rate was determined using equation (2);

$$\text{Burning rate} = \frac{(\text{final length of specimen - initial length of specimen}), \text{m}}{\text{Overall burning time, s}} \tag{2}$$

Thermal Conductivity Test Thermal conductivity was carried out using thermal conductivity analyzer model Anacon. Samples were cut into 160 mm × 160 mm × 30 mm (length × width × thickness). Thermal conductivity was calculated based on equation (3);

$$\text{Thermal conductivity, k} = \frac{tQ}{A\Delta T} \tag{3}$$

where t is the sample thickness (m), Q is the sample conductivity value (W), A is the tested surface area of the sample (m^2) and ΔT is the temperature difference (K) between the hot plate and the cold plate.

Acoustic Test The acoustic test was performed according to ASTM E150 using impedance tube Model SCS9020B/K. The acoustic absorption coefficient (α) is defined as the ratio of the acoustic energy absorbed by the foam ($I_{incident} – I_{reflected}$) to the incident acoustic energy ($I_{incident}$) on the surface and is dependent on frequency. The frequency range was 125 – 4000 Hz.

Scanning Electron Microscopy (SEM) Analysis The SEM analysis was used to study the dispersion of ATH in hybrid composites. The analysis was carried out using the SEM chamber model Phillips XL-30. The dried samples were pre-coated with gold using gold sputter coater model SC500. Observation was made at 500 × magnifications.

RESULTS AND DISCUSSION

MECHANICAL PROPERTIES

Figure 1 shows the trend in compression stress and modulus of PU hybrid composites with 0, 2, 4 and 6 wt% ATH. Addition of 2 wt% ATH increased the compression stress and modulus to 575.2 kPa and 2301.8 kPa respectively but was deteriorated after further addition of the ATH.

The stress put onto the PU system creates energy that is absorbed by the EFB. This energy is transferred to the PU matrix and ATH subsequently and uniformly being dispersed in the system. Addition of rigid particles such as ATH in the PU system leads to an increase in the brittleness of the composites as observed by Dvir et al. (2003). Loading of ATH in the PU system has caused disruption in the PU system. It creates disorder to the cellular structure. The same observation was encountered by Nachtigall et al. (2006) when ATH was blended in polypropylene. There was a tendency for the ATH to weaken the mechanical strength of the composites due to the rigidity nature of the ATH particulates. Khairul Anuar Mat Amin and Khairiah Haji Badri (2007) has reported in their study using kaolinite as filler that the presence of kaolinite disturbed the interfacial adhesion of PU matrix and EFB. These supported the findings in this study where there was a reduction in the compression stress and modulus at 4 and 6 wt% ATH. Further explanation was verified by the SEM micrographs.

Figure 2 shows the SEM micrographs of the control PU and the hybrid PU composites at ATH loading of 2, 4 and 6 wt%. Figure 2(a) shows the structure of the unfilled PU. The micrograph indicated uniform hexagonal cellular structure of PU. At 2 wt% ATH, the ATH adhered to the cell wall together with the EFB. During compression testing, the stress transferred continuously from the matrix to the EFB and to the ATH. This resulted in a uniform distribution

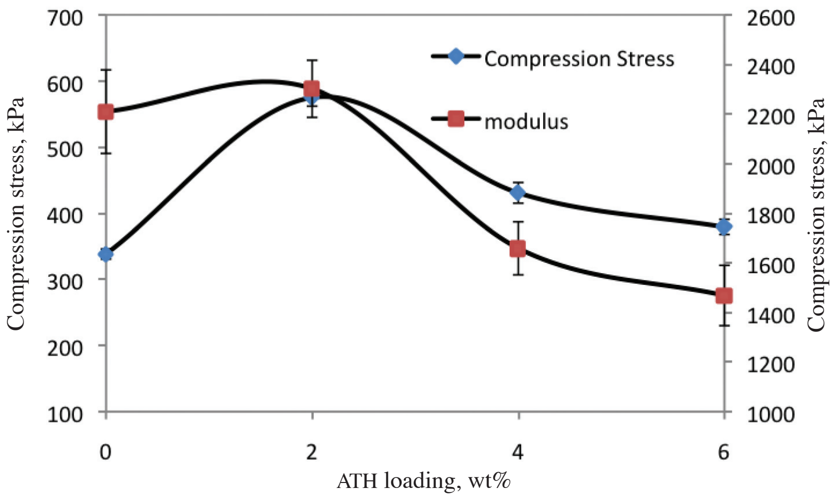
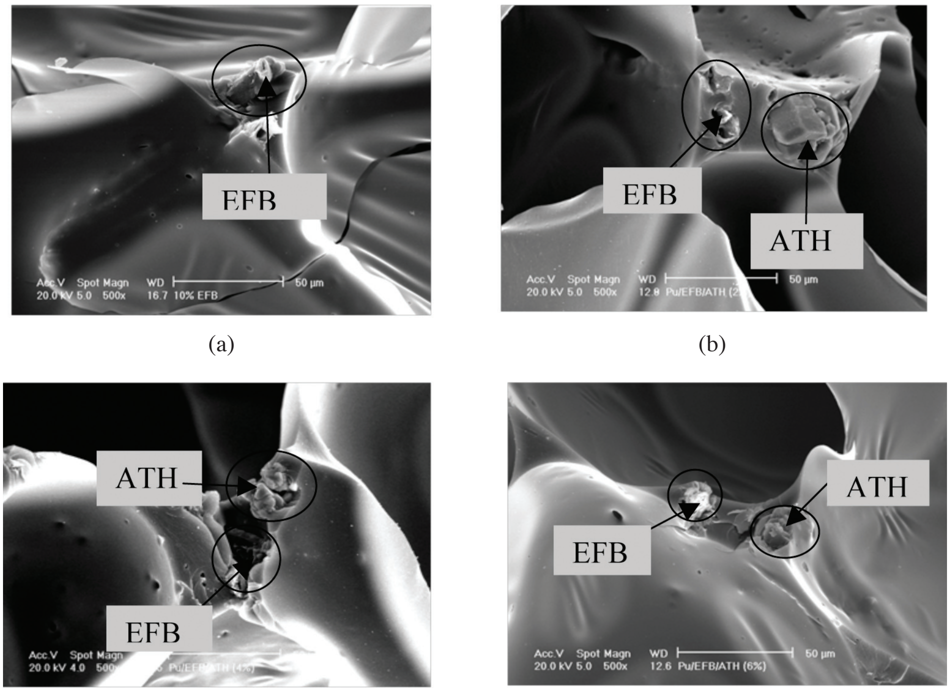


FIGURE 1. The compression stress and modulus of the PU hybrid composite



(a)

(b)

(c)

(d)

FIGURE 2. SEM micrographs of the (a) control PU and the hybrid PU composites filled with (b) 2 wt% ATH (c) 4 wt% ATH and (d) 6 wt% ATH

of the stress. Figure 2(c) and (d) shows ruptured cell walls of the PU composites. These created stress concentration point where it produced discontinuity in the matrix (Khairul Anuar Mat Amin & Khairiah Haji Badri 2007).

BURNING RATE

Figure 3 shows the burning rate of the PU hybrid composites. Control PU showed higher burning rate at 3.30 mm/s. Addition of EFB in the composite increased the burning rate. EFB has porous structure. In this porous structure contains air and oxygen mixture. When flame is in contact with the EFB, it will react with oxygen and combustion occurs. Besides, the nature of PU itself which is flammable also contributes to higher burning rate. When ATH was added to the PU system, the burning rate was lowered. ATH released some amount of water when in contact with heat as shown in (1).

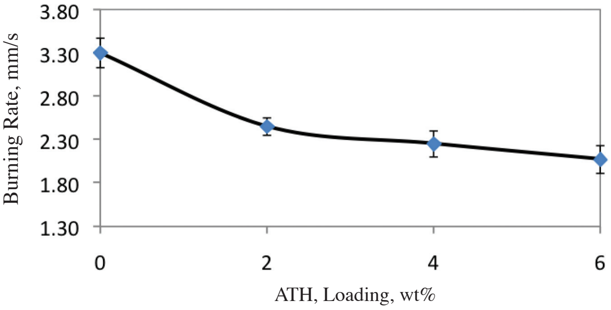


FIGURE 3. Burning rate of the PU hybrid composites

During the burning process, water released from ATH diluted the combustible gases and thus reducing the oxygen availability (Ahmad Ramazani et al. 2008; Nachtigall et al. 2006). Beside this water vapor, production of alumina on the polymer surface prevented the polymer from being in contact with the oxygen by acting as protective layers (Mansour 2000).

THERMAL CONDUCTIVITY

Figure 4 shows the thermal conductivity of the hybrid PU composites at various ATH loading. The thermal conductivity increased with increasing ATH loading in the system but decreased at 6 wt% ATH. This indicated that the addition of ATH in the PU system contributes to poor thermal insulation value (λ-value or k-value). The disability of ATH to dissipate the energy in term of heat flow resulted in higher k-value at higher ATH loading. Benli et al. (1998) reported that incorporation of fine filler particles in the matrix enhanced the thermal conductivity. When heat was introduced to the hybrid composites, ATH as rigid particles absorbed some amount of heat and transferred these heats to the nearby ATH particulate in the system. Modesti et al. (2002) also reported that addition of solid particles in the composites leads to higher thermal conductivity. The thermal conductivity of the hybrid PU system at 6 wt% ATH decreased maybe due to random dispersion of the ATH particles in the PU-EFB matrix as reported by Kumluta et al. (2003). It might also be due to the ruptured cell wall that increased the outward diffusion rate of carbon dioxide and inward effusion rate of air in the PU system. Since air has lower k-value compared

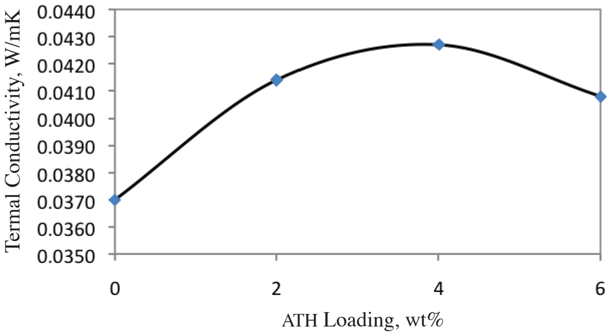


FIGURE 4. Thermal conductivity of the PU hybrid composites

to carbon dioxide, the whole hybrid PU composites exhibited an improved thermal conductivity.

ACOUSTIC PROPERTIES

The acoustic analysis on the hybrid PU composites (Figure 5) shows that at lower frequencies (125-500 Hz), poor sound absorption was observed. The absorption coefficient (α) was the highest at 4 wt% ATH compared to 2 and 6 wt% ATH. All the hybrid PU composites indicated higher absorption coefficient at frequency ranges of 2000-4000 Hz. When the incident sound wave hit the ATH, the sound energy is dispersed in the composites due to the attenuation of air viscosity in the cell pore. Interaction between the vibrated ATH increased the low frequency attenuation thus increase the absorption coefficient (Zhou et al. 2006).

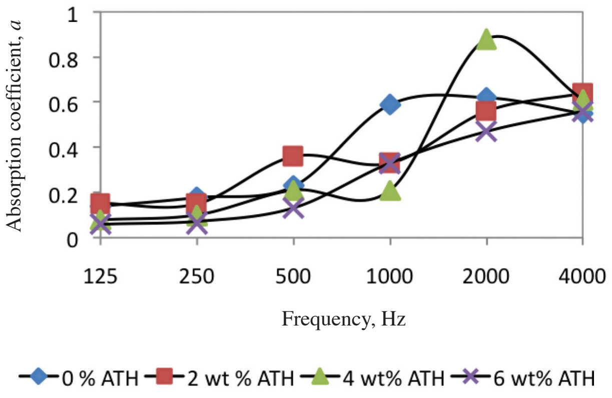


FIGURE 5. Acoustical properties of the hybrid composites

CONCLUSIONS

The incorporation of EFB and ATH in the palm-based polyurethane has been carried out. Their effects on the mechanical, thermal conductivity, acoustical and burning properties of the hybrid PU composites were studied. The hybrid PU composites with 2 wt% ATH showed the highest compression stress and modulus as well as thermal conductivity. However, the acoustic study indicated that loading of ATH at 4 wt% showed the highest absorption coefficient at the range of 2000-4000 Hz. The addition of ATH into the PU matrix had successfully improved the burning rate of the hybrid composites. In general, the addition of ATH into the PU system is able to improve the mechanical, thermal, acoustic and burning properties of the composites. However, treatment of ATH might be necessary to improve its interfacial adhesion with the PU matrix.

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