



تأثير الجرافيت القابل للتمدد كمثبط للحريق على الخواص الحرارية للألواح الليفية متوسطة الكثافة من ألياف نخيل الزيت المرتبطة بالبولي يوريثين المبدئي (الأولي).

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EFFECT OF EXPANDABLE GRPHT AS FIRE RETARDANT ON THERMAL
PROPERTIES OF MEDIUM-DENSITY FIBERBOARD FROM OIL PALM FIBER
CROSS-LINKED WITH PRE-POLYMERIZED POLYURETHANE

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الملخص:

تم استخدام مادة البولي يوريثين أولية البلمرة (pre-PU) كمصفوفة لاصقة في هذا العمل لإنشاء ألواح ليفية متوسطة الكثافة (MDF) تعتمد على ألياف عنقودية فارغة من نخيل الزيت (EFB) بنسبة 60:40. تم استخدام الجرافيت القابل للتوسيع (EG) كمثبط للحريق عند نسب تحميل تبلغ 0، 10، 20، و30 بالمائة من الوزن من إجمالي كتلة المادة المصفوفة، وتراوح حجم ألياف EFB من 500 إلى 700 ميكرومتر. تم استخدام تحليل قياس الوزن الحراري (TGA)، وقياس السرعات الحرارية بالمسح التفاضلي (DSC)، وقياس السرعات الحرارية للقنابل لتقييم معالم الطاقة الحرارية وإطلاق النار. في ظل وجود مستويات تحميل مختلفة من الجرافيت القابل للتوسيع (EG)، أظهرت التجارب الحرارية الشاملة سلوكًا حراريًا معززًا لـ EFB-MDF، والذي ارتبط بزيادة كثافة التفحم في المواد النهائية وانخفاض فقدان المواد. أدت زيادة مستويات تحميل EG إلى تحسين ميكانيكية EFB-MDF، مما أدى إلى ارتفاع ثابت في الصلابة، تليها زيادات في الفقد، ومعامل التخزين، وقيم دلتا tan. توفر دراسات التزجج (DSC) تدهورًا أحادي الطور للمادة بأكملها من خلال إظهار أن EG يتم توزيعه بشكل موحد في جميع أنحاء نظام الراتينج. ومع زيادة مستويات التحميل من 10% إلى 30%، تحولت درجة حرارة التدهور باستمرار نحو قيمة أعلى.

الكلمات المفتاحية: الجرافيت القابل للتمدد (EG)، ألياف EFB، اللوح الليفي متوسط الكثافة، البولي يوريثين الأولي، الخواص الحرارية.

Abstract:

The prepolymerized polyurethane (pPU) was used as the adhesive matrix in this work to create medium-density fiberboards (MDF) based on oil palm empty fruit bunch fibers (EFB) at a 60:40 ratio. Expandable graphite (EG) was employed as the

fire retardant at loading percentages of 0, 10, 20, and 30 weight percent of the matrix's total mass, and the EFB fiber ranged in size from 500 to 700 μm . Thermo gravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and bomb calorimetry were used to assess thermal and fire release energy parameters. In the presence of different loading levels of Expandable Graphite (EG), the thorough thermal experiments showed enhanced thermal behavior of EFB-MDF, which was associated by higher charring density end material and decreased material loss. Increased EG loading levels improved the mechanicals of EFB-MDF, resulting in a steady rise in stiffness, followed by increases in loss, storage modulus, and tan delta values. The glass transition studies (DSC) provide a single phase deterioration of the entire material by demonstrating that EG is uniformly distributed throughout the resin system. As the loading levels increased from 10% to 30%, the deterioration temperature continuously shifted towards a higher value.

Keywords: Expandable Graphite (EG), EFB fiber, Medium density fiberboard, pre-polyurethane, thermal properties.

Introduction

Natural fibers are fibers that are derived from plants, animals, or minerals, and have been used for centuries in various applications such as textiles, ropes, and paper. These fibers are renewable, biodegradable, and environmentally friendly, making them an important alternative to synthetic fibers, which are typically made from petroleum-based chemicals. Natural fibers have been utilized extensively recently as a substitute to the ever-depleting petroleum sources. However, replacing 100% of natural fiber-based production with petroleum-based material may not be an economical solution (Shogren et al. 2019). Finally, merging petroleum and bio-based resources lead to create a cost-effective product with many applications (Redwan 2020). However, present progresses are now concentrating on lessening the use of synthetic fibers by replacing with natural fibers as a respect to the environment; biodegradability and renewability. This leads to the eco-composite material generation. Besides that, it is also being compared to glass fibers, natural fiber reduce dermal and respiratory irritation during handling as well as reducing tool wear. For this reason, alternate reinforcement with natural fiber gained attention. Natural lignocellulosic fibers for example jute, sisal, flax, kenaf and oil palm fiber are among the fibers documented for their role as reinforcement and can

be favorably used for the development of an environmentally friendly composites with good physical properties (Singh & Palsule 2013).

Fiberboard is a type of engineered wood product made from wood fibers, which are processed under heat and pressure to form a dense, solid sheet material. It is used in a wide range of applications, from furniture and cabinetry to construction and packaging. Fiberboard is popular due to its versatility, affordability, and ease of use. It can be produced in various densities and strengths to suit different purposes.. Fiberboards are characterized by density. A medium density fiberboard (MDF) has a specific gravity around 0.50 and 0.80 (density of 31 to 50 lb/ft³). (ASTM Standards D1554-1986). One type of wood-based material normally used in buildings and house furnishings is medium-density fiberboard (MDF). The most important restriction of MDF is its vulnerability to fire hazard and therefore making the material able to resist fire is essential (Alves et al. 2023). Preserving physical and mechanical properties must be taken into consideration when developing flame retardant MDF. When wood is heated, chemical bonds begin to break down at about 175 °C, and the reactions advance as the temperature rises. When heated at 100 °C to 200 °C in without the presence of air, non-combustible products like carbon dioxide, traces of formic and acetic acids and water vapour are formed. Above 200 °C, the carbohydrates break down and tars are produced and flammable volatiles are diffused into the surrounding environment (Shafizadeh 1984). Above 450 C, the manufactures of flammable products are complete. The residue remaining is char (Das et al. 2016). Cellulose decomposes in the temperature ranging from 260 °C to 350 °C, and it is mainly responsible for the production of flammable volatiles. The cellulose thermal degradation can be hastened when water, acids, and oxygen are present. As the temperature rises, the cellulose polymerization degree is further decreased, free radicals appear, and forming carbonyl, carboxyl, and hydroperoxide groups.

Generally, chemicals based flame retardants may influence some properties of materials. It was discovered that flame retardants with a combination of boron lessened the mechanical properties and surface quality of wood panels (Ayrilmis et al. 2020). Commonly, flame retardants do not stop the wood and wood panels from burning. Some of them do surge the temperature where combustion can happen. Thus, the rate at which a fire will spread is reduced due to the improved ignition temperature and the time needed to reach that temperature (Redwan et al. 2015).

Some flame retardants, when in wood, decrease the temperature, causing wood thermal degradation. The result is less combustible pyrolysis gases (and more char) which results in less flaming combustion to spread the flames. Therefore, to increase the combustion performance of wood and wood panels, they must be coated with several flame retardants. When inspecting flame retardants mechanism during fire tests, it was decided that the flame retardants melted completely during high-temperature tests, flowing and covering the whole panel like a lamella. Thus, flame retardants can better the fire panels' performance this way (Lim 2023).

Schafhautl initially documented Expandable Graphite (EG) in the literature in 1841 while examining graphite crystal flakes in a sulfuric acid solution. There have been prior reports on EG's flame-retardant properties in polyurethane coatings. At 25 weight percent loading, the oxygen index rises from 22 to 42 vol.%. EG has been shown to be an effective addition that serves as both a carbonization and blowing agent. An intumescent additive called EG is known to enhance the fire-retardant qualities of a variety of materials, including polyurethane (PU) foam (Duquesne et al. 2003). Given that graphite is a somewhat stable material at room temperature, its expandable quality is crucial to the formulation of fire retardants. The dilatibility and thermal stability of EG are crucial factors when it comes to flame retardant applications. EG is classified as low (between 80 and 150 °C), moderate (between 180 and 240 °C), and high (between 250 and 300 °C) in terms of thermostability. High thermostable graphite will expand at temperatures between 280 and 438 °C, forming a porous physical barrier between the flame and the material to be protected (Zhao et al 2015). Additionally, void areas that enable airflow are created within the char during the formation process, which cools the fire environment (atmosphere) and lengthens the time it takes for the covered cellulosic material to ignite. Generally speaking, research is currently ongoing to determine the kinetics of fire-protected cellulosic materials (Zheng et al. 2019). The current study focused on the effect of flame retardant, namely Expandable Graphite (EG) on the thermal properties of the Medium-Density fiberboard (MDF) prepared via pre-polymerization method.

EXPERIMENTAL

MATERIALS AND PREPARATION

UKM Technology Sdn Bhd provided the palm-based polyol (PKO-p) via its pilot plant located at MPOB/UKM Station in Pekan Bangi Lama, Malaysia. We bought

the crude 4-methylene diphenyldiisocyanate (MDI), also known as Cosmo-polyurethane (Cosmonate M-200), from Cosmo-polyurethane in Port Klang, Malaysia. Merck Sdn Bhd, located in Shah Alam, Malaysia, provided the acetone. Fluka Chemie Sdn. Bhd. was the supplier of polyethylene glycol (PEG200), which has a molecular weight of 200 Da. The source of the oil palm empty fruit bunch fiber (EFB) was Syarikat Seri Ulu Langat in Banting, Australia. China's Action Carbon Co. Ltd. produced Expandable Graphite (EG) in Baoding.

The Ika Werke MF10 heavy-duty grinder was used to refine the dried EFB fiber (EFB), which was subsequently sieved to produce diameters between 500 and 700 μm . PKO-p and PEG200 were combined in 20% acetone to create the resin. Additionally, acetone (20 weight percent) was added to the crude MDI. Separately, the liquids were shaken for 80 seconds at room temperature at 200 rpm in tiny beakers. A 1:2 ratio was employed for the quantity of PKO-p and MDI. Pre-PU, or prepolymerized polyurethane resin, was created as a result.

By combining EG and EFB with pre-PU, medium-density fiberboard (MDF) was created. The pre-PU to EFB ratio was 40:60. Before blending with KF for 60 seconds and hot pressing at 57 $^{\circ}\text{C}$ for 10 minutes at 760 MPa, the flame retardant (EG) was combined with the pre-PU in different weight percentages of 10, 20, and 30%. For additional characterizations, the MDF was cut to the required size using a Seppach circular saw model TS400IS after being conditioned for 24 hours at room temperature.

CHARACTERIZATION

Differential Scanning Calorimetry (DSC)

The Perkin Elmer Model DSC-7 differential scanning calorimeter, which was interfaced to the controller Model 1020, was used to measure the MDFs' glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and heat capacity (C_p). The samples were heated at a rate of 10 $^{\circ}\text{C}$ per minute from room temperature to 250 $^{\circ}\text{C}$ (Polyurethane decomposes at temperatures higher than 250 $^{\circ}\text{C}$) (Fodor et al. 2012). About 10 mg samples were analyzed in a nitrogen gas environment using a standard aluminum pan.

Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer model Shimadzu TGA-50 with a temperature range of 25 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ and a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under a nitrogen gas blanket

was used to assess the thermal stability and weight loss of the MDFs. Samples ranging in mass from 5 to 15 mg were put in an alumina pan holder.

THERMAL PROPERTIES

Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical method that measures the variation in the amount of heat needed to raise a sample's temperature as a function of temperature. As shown in Table 1 and Figure 1, a single glass transition temperature was identified for the EFB-MDF system in this investigation with varying EG loading quantities. The existence of a single glass transition unmistakably indicates the existence of a single miscible compatible system, where the matrix, fiber, and binder systems are highly crosslinked to one another by surface adhesion and partial overlap. Both the soft segment (PKO-p fraction) and the hard segment (MDI fraction) are crucial to the stiffness and flexibility of EFB-MDF.

Table 1 Glass Transition (T_g) values for EFB-MDF and EG/EFB-MDF

Samples	T_g , °C
EFB	54.5
PU	55.2
Control EFB-MDF	55.5
EFB-MDF + 10 % EG	60.2
EFB-MDF + 20 % EG	66.4
EFB-MDF + 30 % EG	70.3

The cross-linked network's density is steadily rising. The single phase behavior with a shift towards a higher temperature zone from 55 °C to 74 °C might be linked to this rise in network density (Thomas et al. 2008). There is a strong correlation between the presence of EG and the temperature change from the lower to the upper region. According to earlier research (Lee et al. 2014) on EFB in the presence of different polymeric resins, including PU systems, it was found that EFB decomposed endothermically as loading levels within the polymeric matrix increased and that there were two distinct glass transition temperatures: one for EFB and one for the polymer matrix. However, EFB-MDF only showed one T_g behavior in the current investigation when EG was present and PU was used as a binder system. The existence of a single T_g indicates that the fiber, resin, and EG filling system are cross-linking and overlapping. With higher EG loading levels, this cross-linking and overlapping become more pronounced, and the existence of a single glass transition suggests that in addition to having distinct phases, the system is miscible with one another.

The system showed a single glass transition temperature, confirming the system's miscibility based on earlier research when composites contain both binary and ternary components. Since EG has no glass transition temperature and is thermally stable up to 305 °C, its presence can be significantly linked to the improvement in phase behavior. The findings are corroborated by a prior work on fiber composites with EG present, which found that greater loading levels of EG caused a change in the glass transition towards a higher temperature (Pereira et al. 2009). Additionally, this behavior implies that a stable dimension is produced inside the structure as a result of significant entanglement of molecules during the formation of the structural network, providing a stabilized phase behavior within the molecules of EFB-MDF together with EG.

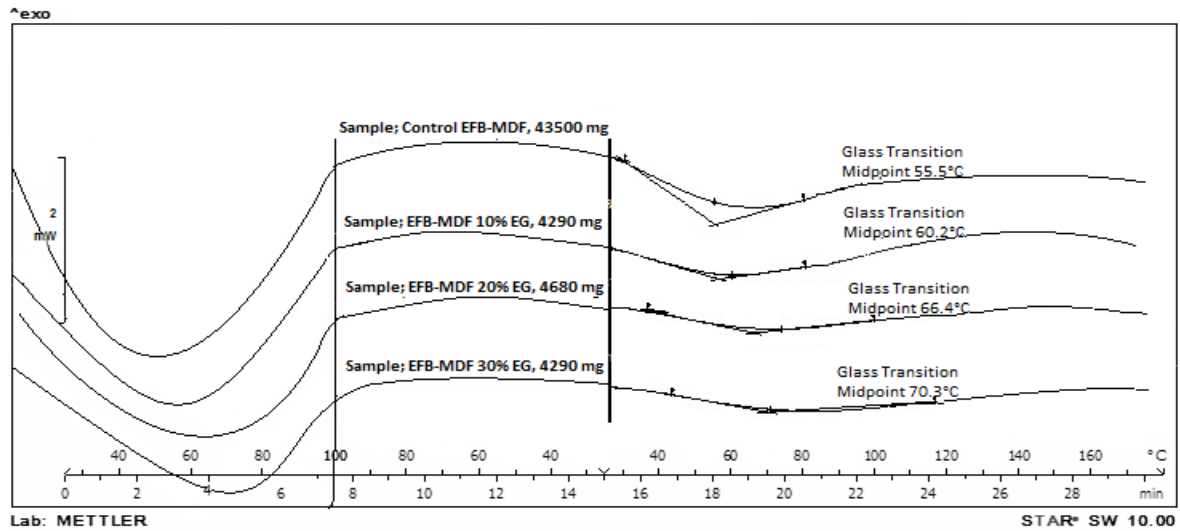


Figure1. DSC thermogram for Control EFB-MDF and EG-filled EFB-MDF

Thermogravimetric Analysis (TGA)

Using a TGA technique, thermal analysis on EFB-MDF in the presence of varying EG loading amounts was further examined. The loss of material weight has moved in the direction of a lower value. In comparison to the EFB-MDF system, this figure indicates a progressive decline in the EG/EFB-MDF system's ultimate decomposition. A decrease in weight loss as EG loading levels rise is a clear indication of EG's uniform dispersion and EFB's encapsulation by the PU matrix, which is followed by a robust cross-linked network structure. Table 2 provides a succinct comparison of EFB-MDF's thermal analysis with and without different loading levels.

Table 2. TGA analysis on EFB-MDF and ATH/ EFB-MDF at 10, 20 and 30% of EG

EG Loading, %	T ₁ °C	Weight Loss, %	T ₂ °C	Weight Loss%	T ₃ °C	Weight Loss, %	Total Weight Loss, %
0	190	9	282	22	328	49	77
10	197	6	282	19	338	49	71
20	204	7	291	19	330	41	66
30	202	5	293	17	356	37	62

The EFB-MDF system's cellulosic content was responsible for the control system's initial 9% weight loss, which was followed by a steady weight loss that indicated the loss of the PU structural backbone (Figure 2). The lack of voids and greater EG dispersion inside the EFB-MDF system were linked to higher loading percentages of EG and higher degradation temperatures. Table 2 illustrates that the early weight loss, T₁, is mostly linked to partial cellulose breakdown and water or moisture loss (Levan & Winandy 2007; Miyafuji et al. 1998). In practice, the first loss for any fiber polymeric resin system that is hydrated is 8–10%, which is equivalent to the loss of whole water molecules from the structural backbone (Gao et al. 2006). But when EG loading levels increased, a drop from 9% to 5% made it evident that MDF's fire qualities had improved. The temperature changes from 190 °C for an unfilled EFB-MDF (PU) system to 202 °C for a 30% filled EFB-MDF (PU) system, indicating this fact.

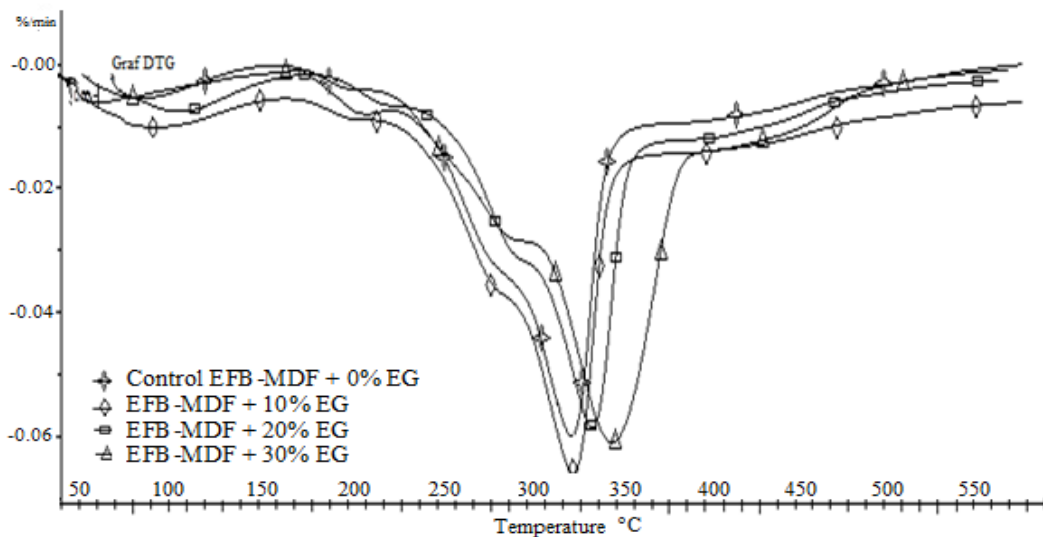


Figure 2. TGA thermograms for EFB-MDF and EG/EFB-MDF at 10, 20 and 30 % of EG

The weight loss at T2 from 200 °C to 280 °C can also be attributed to the breakdown of cellulosic and hemicellulosic components, which is followed by a complete PU degradation. T2 shows a change from a starting temperature of 282 °C to 293 °C. The temperature shift towards higher values is caused by the formation of intermolecular network structures through hydrogen bonding with the EG system, and as a result of intermolecular bonding, the loss weight content is much lower than that of the empty system. This is because structurally, EG degradation starts at 175 °C and proceeds at a very slow rate until 300 °C (Muir et al. 2023).

The final weight loss, represented by T3 depicts clearly the degradation of lignin in the control system. However, less degradation behavior was observed onto the EG/EFB-MDF, associated to enhanced interaction between EG and lignin via intermolecular hydrogen bonding, which helps in material prevention in terms of improved charring density formation (Lu et al. 2016). At higher temperature, most of the cellulose and hemicellulose undergo complete degradation leaving lignin, which is thermally stable, as char and reduces flammable gas formation in dual combination with EG. A constant slow degradation behavior from 355 °C to 515 °C (Figure 2) signifies the charring formation of the material, which is a characteristic feature of EG associated with the bonded lignin material within EFB-MDF (PU) system. An increase in EG loading levels from 10% to 30% was associated with a drop in total weight loss from 77% to 61%, which was followed by an increase in charring density. The material's structural dimensional stability is also linked to this noticeable drop in weight loss from a higher value to a low one. As of right now, EG is widely recognized for its ability to absorb heat and breakdown with a high degree of endothermicity, which results in the generation of less flammable char. The structural features of EG, which also serves as a thermal stabilizer, are strongly associated with an improvement in thermal stability for EFB-MDF structures with higher loading levels of EG.

CONCLUSION

The goal of this study to investigate the thermal properties of medium density fiberboards (MDF) made from renewable biomass Empty fruit bunch fiber (EFB) and polyurethane as binder systems in presence of various loading levels of EG (10%, 20% and 30%). From the detailed studies, it was observed that EG which act as a flame retardant offers improved thermal stability, and better dispersion. The

most important thermal property appeared with a single glass transition temperature along with a shift towards the higher temperature region. All the composites material showed better thermal properties with increased charring density comparatively to unfilled fiber system. This is mainly attributed due to the presence of EG molecule, which itself acts as a flame retardant material by delaying the heating response within the system. Based on the thermal it was observed that EG filler system acts in the gas phase by inhibiting the exothermic oxidation reaction in the flame via radical scavenging thus reduces the energy feedback to the composite surface.

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