Effect of cyclical thermal to mechanical properties of Hybrid Laminate Composites (HLC) with skin recycle polypropylene/natural fiber/halloysite and core PP/KF composites

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Abstract. This research has successfully synthesized six hybrid laminate composites (HLC). These HLC consist of two layers skin composites and one layer of core PP/KF composites. There are sticked with epoxy adhesive by using cold press method. In this research 6 types of skin are used, namely the rPP (recycled polypropylene, HC1); rPP/DVB/PP-g-AA/KF (HC2); rPP/DVB/PP-g-AA/Hall (HC3); rPP/DVB/PP-g-AA/Hall+ZB (HC4); rPP/DVB/PP-g-AA/KF/Hall (HC5) and rPP/DVB/PP-g-AA/KF/Hall+ZB (HC6) composites. The mechanical properties assessment tensile strength (TS) of various HLC before and after cyclic thermal (CT) was done by ASTM D638. While testing the flame retardant: such as time to ignition (TTI) and burning rate (BR) was done by ASTM D635. Heat stability of HLC can be recognized by conducting the CT treatment. It is to determine the effect of fluctuating heat loads on mechanical properties of HLC materials. The TS result of five HLCs (HC2, HC3, HC4, HC5 and HC6) before CT treatment were higher than HC1 (blank HLC). Those five HLC are also able to increase the TTI and reduce the BR compared to HC1. The CT treatment conditions performed at 45 °C as much as 125 times. After CT treatment, the TS values only slightly decline compared to before CT treatment.

1. Introduction

By the development of science and technology, composites design leads to the development of hybrid composites. Hybrid composite is a composite which uses two or more kinds of fillers in a single matrix [1]. One of the means to overcome the weaknesses of the mechanical properties of the composite is to develop a new type of composites, namely Hybrid Laminate Composites (HLC). HLC is a combination of at least two layers of the composite laminate skin and core materials which glued together with an adhesive. The skin is a layer on the HLC surface which coats the core of HLC, Figure 1 [2-4]. Currently, the gluing method used to combine layers of the laminate in the HLC is the most suitable method, because the adhesion is lightweight, it does not require high technology and the stresses distributed more evenly, so it can produce a highly strong HLC [3,5]. One type of adhesive used is an epoxy which has a high adhesion capabilities, robust and heat resistant [4,6]. Generally, the
main properties of the core material are able to increase the thickness of HLC, so that it can improve the mechanical properties without increasing significant weight [2].

The composition of the skin composites to produce HLC must fulfill the criteria, such as has high mechanical properties and high flame resistance [2]. In the automotive industry, composite materials used must have strong mechanical properties, flame retardant (heat stability), and lightweight. The fuel efficiency of the automotive construction must be as light as possible [1]. According to some researchers, improved mechanical properties can be done with the addition of natural fibers such as kenaf fiber (KF) [7-10]. Suharty et al. [11] had synthesized some composites: [rPP/DVB/PP-g-AA/Hall], [rPP/DVB/PP-g-AA/Hall+ZB], [rPP/DVB/PP-g-AA/KF], [rPP/DVB/PP-g-AA/KF/Hall], [rPP/DVB/PP-g-AA/KF/Hall+ZB], which is able to significantly improve the mechanical properties. It is found that cellulose of KF and halloysite (Hall) can interact with PP matrix through coupling compound PP-g-AA and compatibilizer DVB. Other researchers had also reported that natural flame retardant compound such as kaolin, bentonite, montmorillonite and Hall is friendly environment [12-16]. Hand et al. [17] and Rawtani et al. [18] reported that the Hall is a potential inhibitory compound because it has high thermal stability and acts as an oxygen barrier to the formation of flame. Suharty et al. [19] also reported rPP/pineapple-leave fiber/bentonite+ZB composites can improve flame resistance due to the cellulose, bentonite, and zinc borate (ZB) compounds can inhibit the combustion process.

Nowadays, the need of automotive increases every year [20]. However, the supporting material such as metal in nature recently was limited. On the other hand, the availability of fuel is also depleting [21, 22]. To overcome those problems alternative material which has good mechanical properties, high heat stability and light in mass for metal replacement, such as HLC material is needed [9, 22]. Some researchers reported that repeated heating on glass-fiber reinforced concrete (GFRC) and bismaleimede (BMI) carbon-fiber composites below the distortion temperature of the primary material will degrade physical and mechanical properties [23, 24]. Susanto [25] also reported that 10 times CT treatment on GFRC and ramie fiber reinforced concrete (RFRC) below distortion temperature of the main matrix causes thermal fatigue and damage, thereby reducing the mechanical properties of composites. To be able to identify heat stability of materials, the CT treatment under distortion temperature of the main polymer matrix must be performed.

In this study, (1) HLC is made by using skin of rPP/KF/Hall+ZB composites which has been synthesized in our previous work [11] and core PP/KF composites:

\[ \text{a)[rPP/[PP/KF]/[rPP]}; b)[rPP/DVB/PP-g-AA/Hall]/[PP/KF]/[rPP/DVB/PP-g-AA/Hall]; c)[rPP/DVB/PP-g-AA/Hall+ZB]/[PP/KF]/[rPP/DVB/PP-g-AA/Hall+ZB]; d)[rPP/DVB/PP-g-AA/KF]/[PP/KF]/[rPP/DVB/PP-g-AA/KF]; e)[rPP/DVB/PP-g-AA/KF/Hall]/[PP/KF]/[rPP/DVB/PP-g-AA/KF/Hall+ZB]; f)[rPP/DVB/PP-g-AA/KF/Hall+ZB]/[PP/KF]/[rPP/DVB/PP-g-AA/KF/Hall+ZB], (2) \]

The mechanical and inflammability properties of HLC is tested before CT treatment. (3) The CT treatment of HLC materials is conducted under distortion temperature of PP to understand their heat
stability (4) The mechanical properties of HLC after CT treatment is tested, (5) This research will find the effect of CT treatment on mechanical properties of HLC.

2. Methods

2.1. Materials

The starting compounds which belong to pro-analysis grade except mentioned is used without any refining. In this work recycled PP (rPP) used is the cup waste of mineral water packaging. The rPP waste after cleaned up then chopped in 2 x 2 mm. The kenaf fiber (KF) used was bark fiber. It was supplied with Centre of Kenaf Fiber Product in Lamongan Indonesia. The KF after been cut to 5 mm size, then being immersed for 24 hours in NaOH 4%. The halloysite powder was supplied by Applied Minerals Inc., USA. After sieving through 200 mesh, the halloysite powder then calcinated at 800 °C for 1 hour. The core materials PP/KF composites were purchased from Toyota Boshoku, Malang Indonesia. The epoxy A and B pro-technical adhesive were purchased from PT. Jutus Kimia Raya Semarang Indonesia. Other chemical compounds, such as acrylic acid (AA) and divinyl benzene (DVB), xylene derived from Aldrich; while benzoyl peroxide (BPO) and zinc borate (ZB) purchased from E.Merck.

2.2 Synthesize of the HLC

Preparation of six types skin composites (see Table 1) refers to Suharty et al. [11]. Synthesizing of six type of HLC are as follow: (1) Preparation of a specimens skin composite with an area 12 x 12 cm² and the surface made rough, (2) Preparation of specimen core composite with an area 12 x 12 cm² and the surface made rough, (3) Preparation of adhesive by mixing epoxy A and B in ratio 1:1, by sudden, (4) Layer up the surface specimens either skin or core each one with 2 grams epoxy (A+B) by hand lay-up. These layers are allowed to stand for 7 minutes (time starting to pressure), (5) Each specimen glued following skin-core-skin construction and then cold pressed with a load of 3 kN/m² for 24 hours.

| Code | Skin | Core |
|------|------|------|
| HC1  | rPP  | PP/KF|
| HC2  | rPP/DVB/PP-g-AA/Hall | PP/KF |
| HC3  | rPP/DVB/PP-g-AA/Hall+ZB | PP/KF |
| HC4  | rPP/DVB/PP-g-AA/KF | PP/KF |
| HC5  | rPP/DVB/PP-g-AA/KF/Hall | PP/KF |
| HC6  | rPP/DVB/PP-g-AA/KF/Hall+ZB | PP/KF |

2.3 Cyclical Thermal (CT) Treatment, Mechanical, and Inflammability Testing of HLC

Criteria of one time CT with duration 30 minutes are: (1) Heating the sample from the temperature 25 – 45 °C for 4 minutes, (2) then held for 12 minutes at 45 °C, (3) After that, cooled down to 25 °C for 12 minutes, (4) Finally, held at 25 °C for 2 minutes. Cyclic thermal (CT) testing carried out by an automatic cyclic thermal equipment. The CT conditions performed at 45 °C as much as 125 times. Mechanical properties assessment was done by using ASTM D638 and inflammability testing following ASTM D635.

3. Result and Discussion

3.1 Mechanical Properties Test Before CT Treatment

The mechanical properties testing of TS and % elongation can be seen in Figure 2. The TS comparison and comparative % elongation against HC1 before CT treatment can be seen in Figure 3. The TS value of HC1 (which is made from rPP skin, referred as HLC blank) was 41.34 MPa. TS of all
HLCs such as: HC2, HC3, HC4, HC5 and HC6 increased to 5%, 12%, 9%, 22% and 30%, respectively. Percentages elongation of HC1 was 3.6; the %elongation of HC2 and HC3 composites 6%, and 11% decreased, respectively; in the other side, the % elongation of HC4, HC5 and HC6 composites 14%, 8% and 3% increased, respectively.

3.2 The Inflammability of HLC Before CT Treatment

The inflammability test result TTI and BR of HC1-HC6 and their comparison before CT treatment to that of HLC blank can be seen in Figure 4 and 5. The TTI values of HC1 is 3.5 seconds; TTI value of HC2, HC3, HC4, HC5 and HC6 composites317%, 350%,139%, 361% and 392% increased, respectively. The BR of HC1 is 16.7 mm/min; BR of HC2, HC3, HC4, HC5 and HC6 composites 57%, 65%, 49%, 71% and 73% decreased, respectively. The cause of the increasing TTI value and the declining BR value is due to the flame retardants on each skin composites HC2 to HC6. The KF content of the skin and core of HC4 will produce charcoal when it burned. The charcoal acts as a barrier to the entry of oxygen, so the flame formation is inhibited. The flame inhibition also has an effect on the combustion process, to decrease the BR. In the HC2 and HC3, which their skin contains Hall and ZB, in the combustion process, Hall can undergo endothermal reaction and also can produce charcoal as a barrier oxygen [12, 14, 17]. In burning process, ZB produced B$_2$O$_3$ and water vapor to inhibit combustion [19].
3.3 Mechanical Properties of HLC After Cyclic Thermal (CT)

The mechanical properties of TS and % elongation values after CT treatment can be seen in Fig. 6. The TS comparison and % elongation comparative results against blank HLC after CT treatment can be seen in Fig. 7. The effect of 125x CT treatment at temperature 45 °C, for each TS value of HC1, HC2, HC3, HC4, HC5, and HC6 decreased slightly. The decreasing values are 6.5%, 3.2%, 2.8%, 2.5%, 3.3% and 3.9 %, respectively. After CT treatment, the result of mechanical properties as follows: almost all the TS of HC1 to HC6 undergo a slight decline. It is because when there is heating in composites, there will be molecule’s movement. This movement changes the structure of composites and resulting in lower mechanical properties. The composites which undergo heating and cooling process repeatedly can lead to thermal fatigue and damage its structures. It slightly decreases the TS of the composites [25].

![Figure 6](image1.png)  
**Figure 6.** Tensile Strength and Elongation at Break of Various HLC Before and After CT Treatment 125x at 45 °C

The effect of 125x CT treatment at temperature 45 °C, for each % elongation value of HC1, HC2, HC3, HC4, HC5, and HC6 increased slightly. The increasing values are 2.7%, 2.3%, 2.5%, 2.0%, 2.0% and 2.2%, respectively. After CT treatment, the result of % elongation as follows: almost all the TS of HC1 to HC6 undergo a slightly ascending. In the CT treatment, HLC which is heated and cooled repeatedly will cause expansion and contraction. HLC, which made from various raw materials having different expansion and shrinkage coefficients, so that it will degrade the initial structure of HLC, including the elongation, was also changed slightly bigger, but this change is not so significant. Chemically, when the compound is heated the molecules will absorb energy, which lead to the movement of molecules irregularly. The irregularity of molecule will affect the strength of the bonds between the polymer molecules either adhesion or cohesion that it can change the structure of the polymer and cause degradation [26]. Thus, the repeating process of heating and cooling to the composites will lead to different expansion and contraction, therefore the bond strength decreased. This resulted in the bond extension so that the elongation of HLC can slightly increase [27]. The slightly changes in the TS as an effect of CT is due to the raw material of HLC each skin and core contain flame retardant compounds significantly. This can be seen in the high TTI value and low BR values of the various HLC. Thus, the absorption of energy on heating is relatively small and is used in an endothermic reaction of the Hall and the charcoal formation of KF and formation B₂O₃ of ZB, where these compounds inhibit the combustion process.
4. Conclusion
This research has successfully synthesized six types of HLC namely HC1, HC2, HC3, HC4, HC5, and HC6. Their mechanical properties of TS and inflammability of TTI and BR before and after CT was done by using ASTM D638 and D635. Before CT the five of HLC (HC2, HC3, HC4, HC5, and HC6) produced materials which able to increase the TS compared to blank HLC. The TTI and BR of HLC before CT treatment were increasing and decreasing respectively, compared to HLC blank. After CT treatment, the TS values of HLC were slightly decline compared to before treatment.

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