Recycled Polypropylene/Kenaf Fiber/Halloysite (rPP/rNR/KF/Hall) smart composites: The influence of bio-compatibilizer addition on Tensile, Morphological and Heat Combustion Properties

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Abstract. Had been successfully synthesized rPP/DVB/PP-AA/rNR/KF//Hall+ZB smart composite in solution reactive processes with various recycled Natural Rubber (rNR) bio-compatibilizer concentration. The addition of rNR bio-compatibilizer improved the total capacity loading (Hall and KF) filler to reach the optimum concentration. The addition of 3% rNR is capable to increase capacity of total loading filler KF and Hall up to 46% as the optimum condition (KH4). At optimum conditions it can increase the Tensile Strength (TS) and Elongation (Elo) up to 16% and 17% respectively, and decrease the Young Modulus (YM) to 1% compared to that of the composites without rNR (KH1). The rNR plasticizer serves as a bio-compatibilizer that can increase the loading filler capacity and well interaction, finally, it can increase the TS properties. The increase of total loading filler KF and Hall to 46% (KH4) can also improve the inflammability of the composites. The Heat combustion (Hg) of KH1 without rNR was 42.3 kJ/g and at optimum condition the Hg of KH4 increases 4.8%, compared to that of KH1. The time to Ignition (TTI) increases by 6.9%, Burning Rate (BR) decreases by 3.7% and the Heat Release (HR) increases by 2.1% compared to that of the composites without rNR (KH1).

1. Introduction

World car production is increasing every year but on the other hand metal as raw material is depleting. Therefore, some automotive products replace metal materials with composite materials that are strong, lightweight, and combustible [1]. Composites are very attractive materials because, they combine different materials properties in ways not found naturally [2]. The use of 35% lightweight composite in automotive can save around 20% fuel usage [3]. Composites are very suitable to be applied in automotive components such as upholstery, door panels, interiors and car bodies [4]. One of the well-known natural reinforcement is kenaf fiber (KF), which has a high cellulose content thus has high tensile strength, ductile and not brittle [5]. In addition, any clay types can also be used for composite reinforcement. Lee et al. made PP/WF/MMt composites with PP-g-MA coupling compounds internally resulting in composites with TS, MY and high melting temperatures [6]. A combination at least two polymeric materials produces composites that have superior functions and properties than their constituent materials. Fiber material provides a temporary strength of polymer matrix, providing dimensional stability and transfer of shear stress
between fibers [7]. The result is a composite of a strong functional material that can be easily adjusted for a variety of uses [8]. To improve the mechanical properties and flame resistance of a composite can be done in addition together of fiber with clay such as halloysites (Hall) [9]. Ismail and Suryadiansyah [7] made PP/recycled natural rubber (rNR) composites reported to have high elasticity and mechanical properties compared to PP. Elastic composite engineering is one of them with the addition of a plastic such as rubber. Xie et al. made PP/styrene-butadiene-rubber (SBR)/SGF composites produce composites with high elasticity and mechanical properties [10]. Balakrishnan et al. made composites PP/epoxydized natural rubber (ENR)/OMMt [11] and other researcher Wang et al. made PP/EPDM/SGF composites to produce composites with high elasticity and mechanical properties [7]. Riyajan et al. [12] made composites PS/recycle rubber glove (rRG)/sugarcane leaves produced by composites with high elasticity and mechanical properties compared to starting materials. Based on this description, in this study studied the effect of the bio-compatible rNR addition in various concentrations in a composite with Hall and natural fibers fillers: that have strong, lightweight and elastic properties compared to the starting material without plastic rNR.

2. Experimental

2.1 Materials

Recycled polypropylene (rPP) was collected from plastic recycling center in Surakarta Indonesia. The rPP prepared by cleaning up the waste cup and then chopped approximately in 5 mm x 2 mm. KF was obtained from the Kenaf Fiber Processing Center in Lamongan Indonesia. The KF was then overnight alkalized with 4% NaOH, and washed with distilled water and then dried in an oven at 60°C before chopped into 5 mm in sized. The recycle natural Rubber (rNR) was collected from waste natural rubber glove in Surakarta, Indonesia. The halloysite (Hall) clay was supplied by Applied Minerals Inc., USA. The Hall prepared by sieving with a 200 mesh and calcinated at 800°C for an hour. Preparation of rNR, after natural rubber glove cleaned up and dried then was decrosslinked. The crosslinked was done by using two roll mill and then crushed and sieved with a 40 mesh. All chemicals used in this study were pro-analysis from Aldrich; while benzoyl peroxide (BPO) and zinc borate (ZB) purchased from E.Merck.

2.2 Composites Manufacturing Process

Formulations of composites as follow: rPP/20%KF/0%rNR/20%Hall+ZB (KH1), rPP/23%KF/0%rNR/23%Hall+ZB (KH2), rPP/23%KF/1%rNR/23%Hall+ZB (KH3), rPP/23%KF/3%rNR/23%Hall+ZB (KH4), rPP/23%KF/5%rNR/23%Hall+ZB (KH5), and rPP/23%KF/7%rNR/23%Hall+ZB (KH6), composites synthesis are given Table 1. Composites synthesis is reactivity done by solution process in xylene, equipped with a condenser, mechanical stirrer and N2 gas. All starting materials: rPP, DVB, PP-AA, Hall, and KF blended in boiled xylene and mixed perfectly for 1 hour. Acrylate acid or AA is a multifunctional coupling compound that functions as a coupling agent for bonding of non-polar compounds (PP, rNR) with polar compounds (KF, Hall). In order for AA to interact more with non-polar compounds, AA coupling compounds are first converted to PP-AA. The mixture product was then evaporated to release the xylene to form masterbatches (MB’s) composites. The MB’s was hot pressured for 20 minutes at 180 °C to produce the specimen for physical and mechanical test [13].

| Table 1. Formulation of rPP/DVB/PP-AA/rNR/KF/Hall+ZB composites |
|------------------|------|---|---|---|---|
| Code            | rPP | PP-AA | rNR | KF | Hall | ZB |
| KH1             | 65  | 15    | 0   | 20 | 20   | 5  |
| KH2             | 65  | 15    | 0   | 23 | 23   | 5  |
| KH3             | 65  | 15    | 1   | 23 | 23   | 5  |
| KH4             | 65  | 15    | 3   | 23 | 23   | 5  |
| KH5             | 65  | 15    | 5   | 23 | 23   | 5  |
| KH6             | 65  | 15    | 7   | 23 | 23   | 5  |
2.3 Testing of materials
Characterization functional groups of raw materials as well as new material produced were performed using Shimadzu FTIR-8201 PC. Mechanical testing of TS, %Elo and Young Modulus (YM) was carried out using universal testing machine (UTM) by following ASTM D638. The testing of flame resilience of composites in accordance with ASTM D635 to determine the value of time to ignition (TTI), burning rate (BR) and %Heat Release (%HR). Bomb Calorimeter model 1341 Parr was used to measure the heat combustion (Hg).

2.4 Morphology Analyzing
The fracture surface of specimens after TS testing was characterized using SEM-EDX JEOL JSM-6360 LA to analysis morphology, especially on the cross section area of the fracture surface.

3. Results and Discussion
3.1 FTIR Analysis Functional Groups of Composites
The result of FTIR characterization is as follow. (a) In the rPP was obtained absorption at 2953-2839 cm\(^{-1}\) was >CH\(-\) and (>CH\(_2\)) groups and typical methyne group (>CH\(-\)) of PP uptake at 1723 cm\(^{-1}\). (b) Broad absorption at 3433 cm\(^{-1}\) represents a hydrogen bonded of –S-H group of rubber, and at 1630 cm\(^{-1}\) of butadiene rubber (-HC=CH-). (c) Broad absorption at 3458 cm\(^{-1}\) represents a hydrogen bonded of hydroxyl groups of cellulose KF, Hall and –S-H group of rubber. Absorption at 2953-2839 cm\(^{-1}\) was >CH\(-\) and (>CH\(_2\)) groups. Absorption peaks at: 2723 (>CH- typical PP), 1629 cm\(^{-1}\) of butadiene rubber (-HC=CH-), and 1373 cm\(^{-1}\) methyl (-CH\(_3\)) [14,15,16,17]. Absorption at 1730 cm\(^{-1}\) represents absorption of carbonyl groups of ester which were produced between hydroxyl cellulose of KF and carboxylic groups of AA. Absorption at 896-1046 cm\(^{-1}\) shown the Al-O and Si-O groups, representing interaction of Hall and PP in smart composites. It can be seen, that had been occurred the interaction among the starting material to form the new rPP/DVB/PP-AA/rNR/KF/Hall+ZB composites. This is supported by the previous work [18,19,20]. This interaction is expected to result in the mechanical properties and heat combustion better than the starting one.

![Figure 1. FTIR spectra of (a) rPP, (b) rNR, (c) rPP/DVB/PP-AA/rNR/KF/Hall+ZB](image_url)

3.2 Mechanical properties of composites
Testing of mechanical properties was carried out with ASTM D638. To prove the mechanical properties of various (KH1-KH6) composites ASTM D635 is used for testing composites. The result is presented by tensile strength (TS), % Elongation (Elo) and Young Modulus (YM) are presented in Figure 2-7. The effect of adding rNR bio-compatibilizer on mechanical properties...
based on the results of testing with ASTM D638 is as follows: (a) Tensile strength of rPP/KF20%/Hall20%+ZB (KH1) composite formulation without addition of rNR plasticizer was 53.9 MPa, an increase of 76% compared to that of raw material rPP (30.6 Mpa). (b) Meanwhile, the addition of rNR plasticizer achieved the optimum condition of composites rPP/3%rRG/KF23%/Hall23%+ZB (KH4). (c) In the composite formulations of KH2, KH3 and KH4 there was a variation in the increase in rNR concentration as follows: 0%, 1% and up to 3% there was a significant increase in TS, 2%, 5% and 16% respectively compared to KH1 without rNR. (d) However, the composite formulations of KH5 (5% rNR) and KH6 (7% rNR) the TS decreased to 3% and 4% respectively. The increasing of mechanical properties was caused by both KF and Hall act as a reinforcing material [21,22,23].

**Figure 2.** TS values of TPE PP/rNR/KF/Hall+ZB with various rNR concentration.

**Figure 3.** TS percentages comparison to that of their KH1 composite.

**Figure 4.** Elo values of TPE PP/rNR/KF/Hall+ZB with various rNR concentration.

**Figure 5.** Elo percentages comparison to that of their KH1 composite.

**Figure 6.** YM values of TPE PP/rNR/KF/Hall+ZB with various rNR concentration.

**Figure 7.** YM percentages comparison to that of their KH1 composite.

The addition of rubber plasticizer improves softness which results in the ability to increase the total amount of filler receipts by 15%. The increase in fillers has a consequence on the
improvement of mechanical properties: TS up to 16%, Elo up to 17% and a decrease in stiffness down to 1% compared to that of KH1 composites without rNR plasticizer. Increasing the amount of KF filler in a mixture of PP matrices will increase the additive interaction between KF and PP which results in increased tensile. The existence of the rNR will increase the elongation which means the % Elo increases, this will reduce the stiffness (YM).

3.3. Morphologies Analysis
The morphological study carried out after TS testing and then characterized using SEM image especially on the cross section area of the fracture surface as can be seen at Fig. 8.

![SEM of the cross section area of the fracture surface](image)

SEM observations showed that the PP/3% rNR mixture matrix was able to bind the KF reinforcement well so that the TS of PP/3% rNR/23%KF/23%Hall+ZB (KH4) is 63.8 MPa. This KH4 composite strength was higher compared to that of PP/20%KF/20%Hall+ZB (KH1) without rNR plasticizer (53.9 MPa). Thus, the addition of 3% rNR can increase the total capacity loading of fillers 15% and larger reinforcements with better binding strength which reflected the increase of TS to 16% compared to that of KH1 without rNR plasticizer. (1) This is indicated by the presence of PP/3% rNR matrix which is firmly bound to the surface of kenaf fiber (can be seen in the SEM image on points A) and (2) the presence of kenaf fiber fracture near the end of the PP/3% rNR matrix bond (can be seen in the SEM image on points B). (3) In addition, the mixture matrix of PP/3% NR is also able to attach strongly to Hall (can be seen in the SEM image on points C); (4) so that the presence of Hall can function properly as an reinforcing filler which is simultaneously a flame retardant. The addition of rNR bio-plasticizer influences the softness which results in the ability to increase the total amount of filler receipts by 15%. The increase in fillers has a consequence on the improvement of mechanical properties: such as the TS up to 16%, the Elo up to 17% and a decrease in stiffness which was down to 1% compared to that of KH1 composites without rNR plasticizer. Increasing the amount of KF filler in a mixture of PP matrices will increase the additive interaction between KF and PP which results in increased tensile. The existence of the rNR will increase the elongation which means the % Elo increases, this will reduce the stiffness.

3.4. Heat Combustion, TTI, BR, and %HR of rPP/DVB/PP-AA/rNR/KF/Hall+ZB
To understand the heat combustion values of rPP/DVB/PP-AA/rNR/KF/Hall+ZB (KH1, KH2, KH3, KH4) composites, its carried out heat combustion testing and also to determine the influence of rNR bio-compatibilizer. The results of heat combustion (Hg) composites (KH1-KH6) using Bomb Calorimeter are presented in Fig. 9 and 10. The Hg of rPP raw material was 45.67 kJ/g. The Hg of rPP/KF20%/Hall20%+ZB (KH1) composites at optimum condition without rNR plasticizer were 42.3 kJ/g, it decreases 7.4% compare to that of rPP. The effect of adding rNR bio-compatibilizer on heat combustion (Hg) is as follows: the Hg of rPP/rNR0%/KF23%/Hall23%+ZB (KH2) composite formulation with addition of 0%rNR plasticizer was 41.3 kJ/g, a decrease 2.4% compared to that of KH1 without rNR. However, in the composite formulations of KH3, KH4, KH5 and KH6 there was containing a variation in the rNR concentration as follows: 1%, 3%, 5%,
and 7% there was a significantly increase of the Hg, 2.4%, 4.8%, 9.5%, and 14.3%, respectively, compared to KH1 without rNR.

To prove the inflammability of various (KH1-KH6) smart composites it performed resistance combustion testing. The method horizontal burning of ASTM D635 is used for testing composites. The result is presented by the time to ignition (TTI), the burning rate (BR) and % Heat Release (%HR), which can be seen in Figure 11-16.

**Figure 9.** Hg values of TPE PP/rNR/KF/Hall+ZB with various rRG concentration.

**Figure 10.** Hg percentages comparison to that of their KH1 composite.

**Figure 11.** TTI values of TPE PP/rNR/KF/Hall+ZB with various rRG concentration.

**Figure 12.** TTI percentages comparison to that of their KH1 composite.

**Figure 13.** BR values of TPE PP/rNR/KF/Hall+ZB with various rRG concentration.

**Figure 14.** BR percentages comparison to that of their KH1 composite.
The addition of rNR as bio-plasticizer influences the softness which results in the ability to increase the total amount of total filler receipts by 15%. The increase in fillers has a consequence on the improvement of heat combustion. In the presence of 23% KF and 23% Hall+ZB (KH4) it increases Hg to 4.8%, this because KF and Hall+ZB can inhibit oxygen in the burning process. Cellulose fibers of KF during the combustion process formed charcoal as a barrier that prevents the entry of oxygen at the surface. The Hall undergo endothermic reaction which can absorb heat energy during the combustion process takes place, while ZB can release water vapor to cool the system [24,25,26,]. The synergy of these three components causing the flame resistance of the composite rPP/KF/rNR/Hall+ZB (KH4) increased significantly. The TTI, BR and %HR of the rPP/KF20%/Hall20%/+ZB (KH1) composites without rNR plasticizer was 9.23 second, 9.42 mm/mins and the %HR is 73. In general, the presence of rNR in composites will accelerate combustion. The higher the rNR concentration the fuel resistance decreases, because of the nature of combustible rubber. However, the presence of KF and Hall is able to withstand these flammability. Meanwhile, the addition of 3% rNR plasticizer achieved the optimum condition of composites rPP/rRG/KF23%/Hall23%+ZB (KH4). The presence of 5% ZB as fire retardant additive can also inhibited TTI and also slow down the BR. The ZB compound if burned is also formed B2O3 which is moist and form a stable charcoal. Water that is released by ZB during combustion can cause charcoal to form a foam that inhibits combustion, this is supporting by some previous work [2,22,27].

4. Conclusion
The compositions of synthesis rPP/DVB/PP-AA/rNR/KF/Hall+ZB by using 3% (w/w) rNR plasticizers to reach the optimum condition can increase total input capacity (KF+Hall) is 15% (w/w. The increased 15% of total loading filler capacity can increase the TS and % Elongation to 16% and 17% respectively and decrease young modulus (YM) to 1% compared to that of the optimum condition without rNR plasticizers (KH1). It can also improve the Heat Combustion 4.8% compared to that of KH1. The fuel resistance of composites also better as follow: increasing TTI by 6.9%, decreasing BR to 3.7%, and %HR increasing to 2.1% compared to that of the optimum conditions without rNR plasticizers (KH1).

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