Blend of recycle polypropylene/kenaf fiber/recycle natural rubber/montmorillonite: the effect of natural rubber plasticizer against tensile strength and burning rate properties of smart composites

Neng Sri Suharty¹,*, Hanafi Ismail², Kuncoro Diharjo³, Desi Suci Handayani¹, Alfia Uke Tahara¹, Alifah Nurlita Sari¹

¹Chemistry Department, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir Sutami 36A Surakarta, Indonesia
²School of Materials and Mineral Resources Engineering, Engineering Campus, University Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia
³Faculty of Engineering, Sebelas Maret University, Surakarta, Indonesia
* Corresponding author: nsuharty@yahoo.com

Abstract. It has been synthesized smart composites from recycle polypropylene (rPP), kenaf fibre (KF), montmorillonite (MMt), Zinc Borate (ZB) and recycle natural rubber (rNR). The composites were synthesized through reactively solution method, using coupling agent PP-AA and crosslinker DVB. The addition of rNR plasticizers acting as bio-compatibilizer will produce softer composite. It will improve the elasticity by increased of percentages elongation properties. Soft composite can rise input capacity filler to reach the optimum condition. The better of loading capacity will improved mechanical (tensile strength, TS) and physical (inflammability) properties. At the optimum condition, the composites can increase tensile strength (TS), time to ignition (TTI), and decrease young modulus (YM), burning rate (BR) compared to that of the optimum composite without rNR plasticizers.

Keywords: smart composites, recycle polypropylene, recycle natural rubber, montmorillonite, plasticizer, kenaf fibre

1. Introduction
In the time being, the world's automotive needs are increasing every year, however, the availability of metals as raw materials is running low [1]. Besides that, the production of petroleum fuels is also decreasing. Therefore, it is very urgent to obtain an alternative composite material that is strong, lightweight and has high fuel resistance as a metal substitute. The use of 35% lightweight composite in the automotive can save fuel usage by 12-20% [2]. Previous researchers have reported that various thermoplastics such as LDPE (Low Density Poly Ethylene), HDPE (High Density Poly Ethylene), PP (Poly Propylene) and recycled Poly Propylene (rPP) can be used as polymer matrix for composite manufacturing [3-6]. Polypropylene is a plastic used widely in various applications such as electronic devices, transportation and packaging [7, 8]. Polypropylene in the packaging of mineral water waste overflow and pollute the environment, it can be used as a polymer matrix [6, 9]. The engineering of composite materials by adding various fillers both fibre and clay in the polymer matrix will improve the mechanical properties and burn resistance. Addition of short glass fibre (SGF) and short carbon fibre (SCF) in PP composites can improve mechanical properties [10]. PP composite with pine apple fibre...
(PaF) filler or LDPE composite with kenaf fibre (KF) filler can improve mechanical properties while also increasing fuel resistance \[11, 12\]. Beside using fibre filler, the addition of montmorillonite (MMt) to PP composites is also able to improve mechanical properties and fuel resistance. Other reinforcing material that has been used by previous researchers is clays \[13-15\]. Any clay other than as a reinforcing material can also act as flame retardants. Shehata et al. \[16\], synthesized a composite of polypropylene and kaolin to produce a composite that has high flame resistance. Du et al. \[17\] make a composite of polypropylene and halloysite clays produce a composite that has high flame resistance. To further improve the mechanical properties and resistance, a softener can be added which can increase the input capacity of filler \[18\]. This research synthesized: (1) rPP/KF/MMt+ZB composite by using the rPP as a matrix, divinylbenzene (DVB) as a crosslinker and PP-AA as a coupling agent and double filler KF and MMt, (2) rPP/rNR/KF/MMt+ZB composite containing various rNR plasticizer concentration. The composites containing rNR plasticizer will provide soft properties. This increases the capacity filler loading resulting in increased mechanical properties and fuel resistance.

2. Methods

2.1. Materials

Recycled polypropylene (rPP) was collected from plastic recycling centre in Surakarta Indonesia. The rPP prepared by cleaning up the waste cup of mineral water and then chopped approximately in 5 mm x 2 mm. KF was obtained from the Kenaf Fibre 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 montmorillonite (MMt) clay was obtained from Soka tile Kebumen Indonesia. The MMt prepared by crushed and sieved with a 200 mesh sieve and calcined at 800°C for an hour. The recycle natural Rubber (rNR) was collected from waste natural rubber glove Surakarta, Indonesia. Preparation of rNR, after natural rubber glove cleaned up and dried then was decrosslinked. The cross-linked was done by processing used 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: 80rPP/20KF/0rNR/20MMt+/5ZB (KM1), 80rPP/23KF/0rNR/23MMt+/5ZB (KM2), 80rPP/23KF/1rNR/23MMt+/5ZB (KM3), 80rPP/23KF/3rNR/23MMt+/5ZB (KM4), 80rPP/23KF/5rNR/23MMt+/5ZB (KM5), and 80rPP/23KF/7rNR/23MMt+/5ZB (KM6), composites synthesis are given table 1. Composite synthesis is reactively done by solution process using xylene, equipped with a condenser, mechanical stirrer and N\textsubscript{2} gas. All starting materials: rPP, DVB, PP-AA, MMt, and KF solved in boiled xylene and mixed perfectly for 1 hour. The mixture product was then evaporated to release the xylene to form masterbatches (MB’s) composites. The MB’s was hot pressed for 20 minutes at 180°C to produce the specimen for physical and mechanical test \[6\].

Table 1. Formulation of rPP/rNR/KF/ MMt+ZB composites.

| Ingredients | Composites (phr) |
|-------------|------------------|
|             | KM1  | KM2  | KM3  | KM4  | KM5  | KM6  |
| rPP         | 80   | 80   | 80   | 80   | 80   | 80   |
| rNR         | 0    | 0    | 1    | 3    | 5    | 7    |
| KF          | 20   | 23   | 23   | 23   | 23   | 23   |
| MMt         | 20   | 23   | 23   | 23   | 23   | 23   |
| ZB          | 5    | 5    | 5    | 5    | 5    | 5    |
2.3. Testing of materials
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).

3. Results and Discussion

3.1. FTIR Analysis Functional Groups of Composites
The result of FTIR characterization on PP was obtained typical methine group (>CH-) of PP uptake at 1723 cm\(^{-1}\) as shown in Fig. 1. In the PP/DVB/PP-AA/rNR/KF composites, the typical uptake of rPP is the >C-H- bond of methine group at 1723 cm\(^{-1}\) and vibration stretching of carbonyl group of ester (>C=O) at 1730 as a binding result between –OH group cellulose of KF with carbonyl (>C=O) of acrylic acid (AA) [6] and absorption at 1618 cm\(^{-1}\) indicates >C=C< butadiene of rubber [19-21]. In composites of PP/DVB/PP-g-AA/rNR/MMt+ZB, functional group of Al-Ostr. can be indicated as the absorption of Al-OH at 867 cm\(^{-1}\), absorption of Si-Ostr. at 1088 cm\(^{-1}\), and Si-O-Si uptake at 486 cm\(^{-1}\) indicates the presence of MMt with the main content of SiO2 and Al2O3. The broad vibration stretching of O-H bond at 3460 cm\(^{-1}\) that indicate hydrogen bond of >Al-OH of MMt. This is supported by the previous research [22, 23]. From the results of FTIR spectra analyses mentioned above, the composites using raw materials of rPP, rNR, PP-g-AA, KF and MMt have been clearly indicated.

![FTIR spectra](image)

**Figure 1.** FTIR spectra of (a) rPP, (b) PP/DVB/PP-g-AA/rNR/KF, (c) rPP/DVB/PP-g-AA/rNR/KF/MMt+ZB.

3.2. Mechanical properties of composites
The result is presented by tensile strength (TS), % Elongation (Elo) and Young Modulus (YM) are presented in figure 2-7. The TS values, Elo and YM composites of rPP/KF20%/MMt20%+ZB (KM1) were 56.9 MPa, 17.5% and 325 MPa, respectively. Meanwhile, the addition of 3% rNR plasticizer achieved the optimum condition of composites rPP/rRG/KF23%/MMt23%+ZB (KM4). There was an
increase in total filler by 15% compared to without rNR (KM1). The composite can increase the mechanical properties of TS by 14%, elongation by 20% and reduce YM by 5%. The increasing of mechanical properties was caused by both KF and MMt act as a reinforcing material [14, 24, 25].

Figure 2. TS values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

Figure 3. TS percentages comparison to that of KM1 composite

Figure 4. Elo values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

Figure 5. Elo percentages comparison to that of KM1 composite

Figure 6. YM values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

Figure 7. YM percentages comparison to that of KM1 composite.

The existence of a reinforcing material in the form of fibres within the polymer matrix serves to hold the burden that has been transferred from the matrix to the fibres. Chemically, KF have polar groups
such as -OH of cellulose are able to interact chemically with methine group of rPP through a coupling compound PP-AA [8]. Furthermore, the presence of MMT clay reinforcing material that has a layer of type 2:1 can improve the mechanical properties. It is caused by the geometry of the clay in the polymer matrix can be distributed both intercalation and exfoliation [26, 27]. Judging from the chemical side, MMT clay has a layer in the form of Si-O tetrahedral and octahedral layers of Al-OH which are capable of interacting with polar groups on a polypropylene methine through the coupling compound PP-AA. Maximum interaction between KF and MMT with PP matrix will lead to increased mechanical properties [8].

3.3. Inflammability properties
To prove the inflammability of various (KM1-KM6) smart composites 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 8-13.

**Figure 8.** TTI values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

**Figure 9.** TTI percentages comparison to that of KM1 composite.

**Figure 10.** BR values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

**Figure 11.** BR percentages comparison to that of KM1 composite.
Figure 12. %HR values of TPE PP/rNR/KF/MMt+ZB with various rNR conc.

Figure 13. %HR percentages comparison to that of KM1 composite.

The TTI, BR and %HR of the KM1 composites without rNR plasticizer was 9.1 second, 10 mm/mins and the %HR is 71. 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 MMt is able to withstand this flammability. Meanwhile, the addition of 3% rNR plasticizer achieved the optimum condition of composites KM4. There was an increase in total filler by 15% compared to without rNR (KM1). The composite can increase the TTI by 2.7%, decreasing BR by 1.9% and increasing HR to 1.5%. Cellulose fibres of KF during the combustion process formed charcoal as a barrier that prevents the entry of oxygen at the surface. The MMt undergo endothermic reaction which can absorb heat energy during the combustion process takes place, while ZB can release water vapour to cool the system [13, 25, 28]. The synergy of these three components causing the flame resistance of the composite KM4 increased significantly. The presence of 5% ZB as fire retardant additive can inhibited TTI and also slow down the BR. The ZB compound binds some water when its burnt will release the water vapour. ZB 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 [24, 28].

4. Conclusion

The compositions of synthesis rPP/KF/rNR/MMt+ZB by using 3% (w/w) rNR plasticizers to reach the optimum condition can increase input capacity 7.5% (w/w) of KF and 7.5% (w/w) of MMt. The increased 15% of total loading filler capacity can increase the TS to 14%, increase % elongation by 20%, and decrease young modulus (YM) to 5% compared to that of the optimum condition without rNR plasticizers (KM1). It can also improve the fuel resistance of composites: increasing TTI by 2.8% and decreasing BR to 1.9% compared to that of the optimum conditions without rNR plasticizers (KM1).

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