

Combustion Resistance and Tensile Strength of Recycled Polypropylene Modified Multifunctional Agent Composites with Kenaf Fiber and in the Presence of Kaolin and Zinc Borate

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Abstract. Had been synthesized different composites from recycled polypropylene (rPP) using Kenaf Fiber (KF), commercial Kaolin (comKao) and zink borate (ZB). In the optimum formula with ratio rPP/KF = 8/2 (w/w), PP modified multifunctional agent AA, crosslinker DVB and kaolin concentration 20% of different composites are measured their combustion resistance and tensile strength. The rPP/KF/comKao/ZB composites materials have a combustion resistance and the mechanical properties better than the starting materials. The burning rate of rPP/KF/comKao/ZB composites according to ASTM D 635 reduced to 77%. The heat combustion of rPP/KF/comKao/ZB decreased to 36%. The tensile strength of rPP/KF/comKao/ZB composites according to ASTM D 638 raised to 90%. The modulus Young of rPP/PaF/comKao/ZB composites increased to 947%.

Keywords: Polypropylene; kenaf fiber; kaolin; composites; multifungtional agent; zink borate

Introduction

Nowadays, metal demand for automotive manufacture is increasing, meanwhile metal resources from nature is decreasing. Moreover, mineral fuel is also getting less, so that the use of fuel for vehicle must be used as efficient as possible. This can be overcome by designing the lighter mass vehicles using composites material. The use of composite materials in automotive vehicles can replace metal components. The lighter mass vehicles which consume the same amount of fuel can accommodate the greater loads. This reflects the vehicle saving fuel exploitation. Therefore, the design of new materials for vehicle instead of metal (such as composite) has to be done urgently. Composites used as

substitute of metal for automotive components are based on its high mechanical strength and combustion resistance [13].

The plastics, especially polypropylene (PP), as thermoplastic polymer is often used for the manufacture of composites such as household appliances and automotive component. It is also used in other industrial applications such as in mineral water packaging which contributes to a large percentage of household waste and it is affecting the environment pollution because PP is non-degradable materials [4-9]. This overflowing of polypropylene packaging waste (recycled PP, rPP) in Indonesia disturbs environmental conservation. To overcome this problem, rPP should be transformed into a new useful material such as composite. Yet, composite itself is not degradable. It should be combined with some other renewable resources, such as kenaf fiber [10-12]. The utilization of renewable resources such as natural fiber KF filler into PP matrix is being actively pursued to improve mechanical properties as well as biodegradable composites [13,14]. This composite which formed from rPP is flammable. So to be able to produce inflammable composite, flame retardant should be added. Previous researchers reported that the addition of clay in the composites are not only improving the mechanical strength but also increasing combustion resistance [15-17]. Various types of clay, such as bentonite and kaolin with high quality are abundant in some parts of Indonesia. Flame retardancy can be achieved by the disturbing of the burning process at any of these stages that can cause the termination of the process before actual ignition occurs [1,5]. The addition of nano CaCO_3 and ammonium polyphosphate (APP) at thermoplastic PP matrix can reduce the burning rate as 30% [18]. In the presence of nano CaCO_3 and DAP at rPP/KF with AA as coupling compounds and DVB as crosslinker can reduce the burning rate as 54% [1]. The addition of kaolin and boric acid on bisphenol epoxy resin matrix can extend the burning time [2,19,20]. Polyvinyl acetate (PVAc) composite with the addition of kaolin and $\text{Mg}(\text{OH})_2/\text{ZB}$ can improve the thermal stability [21].

Chemically polypropylene has non-polar reactive methine functional group. It is able to react with hydroxyl cellulose of KF if it is used with PP modified acrylic acid (PP-AA) coupling agent. In this work, KF was used either as filler or reinforcement in rPP/PP-AA/KF composite. To improve its mechanical properties, divinylbenzene (DVB) was used as compatibilizer in rPP/DVB/PP-AA/KF composite. To produce composite with inflammability properties kaolin which has and Si=O polar functional groups is added [11,16,22-24].

In this research, polymer matrix composites of rPP with KF reinforcement, kaolin fire

retardant and ZB as a fire retardant additive had been synthesized. The effect of KF and kaolin on the mechanical properties and combustion resistant of composites were investigated.

Experimental

All chemicals as starting compounds were in pro-analysis grade except mentioned, and used without any further purification. The rPP was obtained from waste drinking water cup. After washed and dried then the rPP samples were chopped in 2×2 mm. The KF was immersed in 0.4% NaOH solution for 24 h to obtain alkalized KF. Then KF was dried in an oven at 40°C and cut into 5 mm in size. The clay as natKao and comKao were purchased from local chemical company. Clay powder after sieving to make 200 mesh sieved and then calcinated at temperature of 800°C for 1 h in the furnace and allowed to stand for 24 h [25].

Characterization of composites samples were performed by using: 1) hot press equipment to prepare the specimens; 2) Tensometry to determine the tensile strength (TS) and Young's modulus (YM) in accordance with ASTM D638; 3) infrared spectroscopy to determine the functional group; 4) X-ray diffraction (XRD) to determine the type of crystal and kaolin interactions that occur within the polymer matrix, and 5) Horizontal burning method to perform flammability test time to ignition (TTI) and burning rate (BR) in accordance with ASTM D635; and 6) Bomb Calorimeter to measure heat combustion.

The synthesis of rPP/DVB/PP-AA/KF/natKao and rPP/DVB/PP-AA/KF/comKao with and without ZB composites is was reactively done in xylene medium by using starting materials: rPP, KF, PP-AA, DVB, natKao, comKao, with and without zinc borate additive. The formulation of bio-composites compounding is given in Table 1.

Table 1. The formulation compounding of various composite rPP/KF/kaolin with and without ZB.

Ingredients (phr)	Composites					
	C1	C2	C3	C4	C5	C6
rPP	100	80	65	65	65	65
KF	-	20	15	15	15	15
natKao	-	-	20	20	-	-
comKao	-	-	-	-	20	20
ZB	-	-	-	5	-	5

The flammability of the composites produced by formula C1-C6 is was tested in accordance to ASTM D635 in order to determine their flammability from the time to ignition and burning rate. When the burning reached $L = 25$ mm, the burning time was started to be counted and finished when length 100 mm was reached. Thus, burning rate can be calculated by using the following equation:

$$BR \text{ (mm/min)} = 60L/t \quad (1)$$

where L = length burnt specimen is 75 mm

t = burning time in sec.

The highest TTI and the lowest BR values showed that the material has poor flammability.

Results and Discussion

Structure interaction studies of composites

The structure of a formed rPP/DVB/PP-AA/KF/comKao+ZB composite was revealed from the infrared spectra for its specific functional groups (Fig. 1) and the uptake diffractogram which has specific crystal peaks of XRD at 2θ with specific crystal field (Fig. 2).

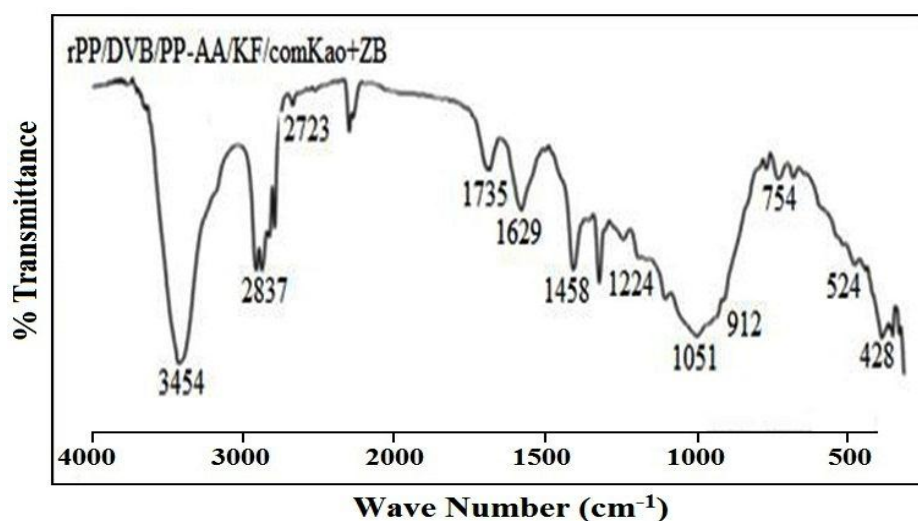


Figure 1. FTIR spectra of rPP/DVB/PP-AA/KF/comKao+ZB.

Based on the FTIR spectra in Fig. 1, each functional group of rPP/DVB/PP-AA/KF/comKao+ZB composites can be analyzed. The IR spectra show the absorption hydroxyl bonding ($-OH$) of Al-OH kaolin overlapping with hydroxyl bonding ($-OH$) of cellulose KF is at 3453 cm^{-1} [7,11,26]. Absorption methylene ($-CH_2-$) stretching is at 2837 cm^{-1} , absorption methyne ($>CH-$) of PP is at 2723 cm^{-1} , and absorption carbonyl ($>C=O$) ester group of AA and cellulose is at 1735 cm^{-1} [11,26]. Absorption vinyl ($>C=C<$) is at

1629 cm^{-1} , absorption methylene ($-\text{CH}_2-$) bending of PP and cellulose is at 1453 cm^{-1} . Absorption of B-O stretching is at 1224 cm^{-1} , absorption of Si-O and Si-O-Al is at 1051 and 524 cm^{-1} , respectively [7,27]. Absorption of B-O bending is at 754 cm^{-1} , absorption of Zn-O-Al is at 428 cm^{-1} [28,29]. From the functional group analysis shows that chemical interaction between PP, PP-AA, cellulose, kaolin and ZB had formed inside rPP/DVB/PP-AA/KF/comKao+ZB composites. This interaction can improve its mechanical properties and durability of fuel better than the PP raw material [21].

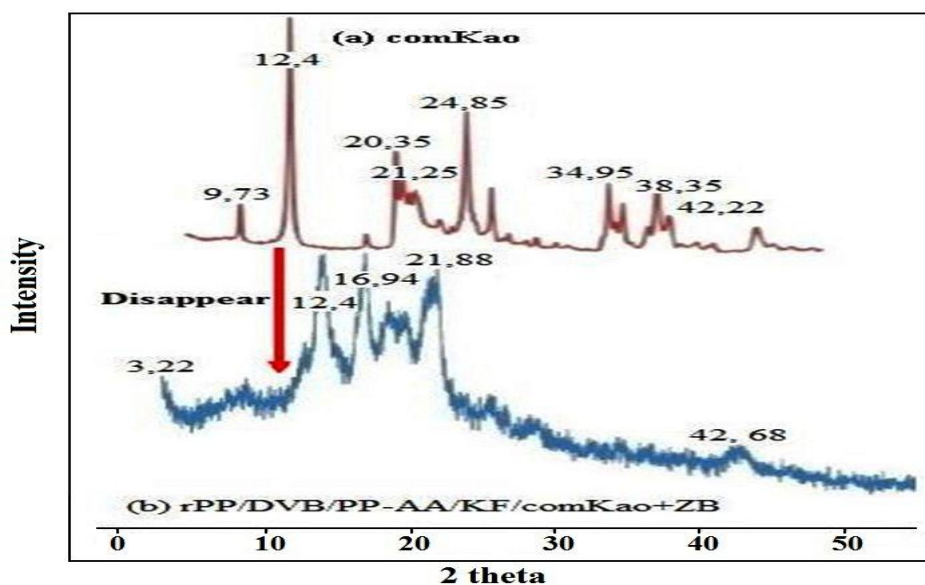


Figure. 2. XRD Diffractogram of rPP/DVB/PP-AA/KF/comKao+ZB.

The kaolin has a characteristic diffraction peaks at 2θ 12.41°, 20.21°, 25.49° [25] and the diffraction peaks are shown in Fig. 2a. After comparison with the data from the ICDD kaolin shows three main diffraction peaks at diffraction angle 2θ of 12.37°, 19.85° and 24.89° where correspond to d -basal spacing of each is 7.14 Å, 4.46 Å and 3.57 Å with a crystal form d_{001} , d_{002} and d_{020} . Diffraction peaks at 12.37° with d -basal spacing of 7.14 Å is the typical peak of kaolin with crystal form d_{001} [30,31].

Fig. 2b is the diffractogram of the composite rPP/DVB/PP-AA/comKao+ZB which displays the peaks at 2θ of 15.02° and 16.84° correlated with d -basal spacing of 5.89 Å and 5.26 Å, according to ICDD owned rPP. Diffraction peaks of kaolin are shown at 2θ of 9.73°, 19.66°, 21.51° and 42.62° correlated with basal spacing is 9.08 Å, 4.52 Å, 4.12 Å and 2.12 Å. However, kaolin which has a characteristic peak at 2θ of 12.37° correlated with basal d -spacing 7.14 Å crystal form d_{001} is disappearing on diffractogram rPP/DVB/PP-AA/comKao+ZB composite. The disappearing of this peak indicates that

kaolin well disperse into the rPP and then form the exfoliate interaction composite [31]. This exfoliate interaction of kaolin can improve its mechanical and inflammability properties of the composites [7,32,33].

Mechanical properties

The results of mechanical test composites (C1-C6) of tensile strength (TS), can be seen in Fig. 3.

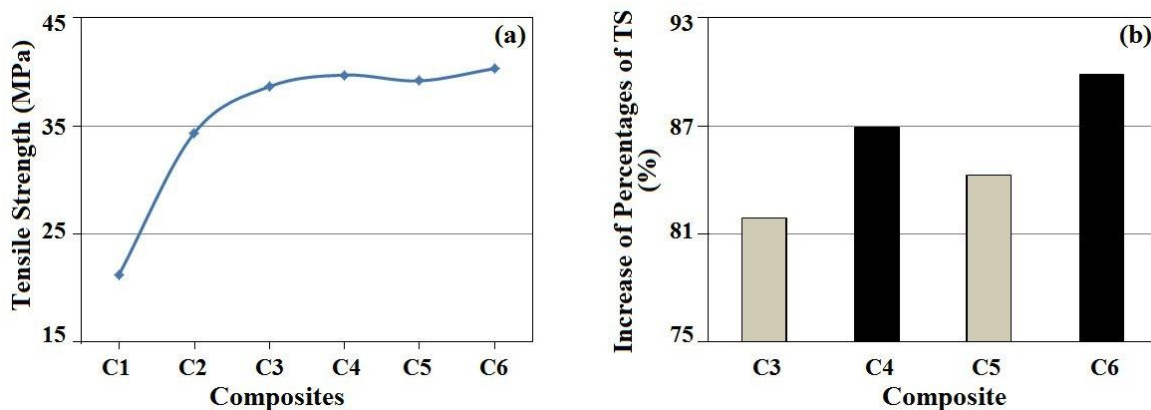


Figure. 3. (a) Tensile strength (TS) of different composites: rPP (C1), rPP/DVB/PP-AA/KF (C2), rPP/DVB/PP-AA/KF/natKao without (C3) and with ZB (C4), rPP/DVB/PP-AA/KF/comKao without (C5) and with ZB (C6); and (b) TS percentages comparison of rPP/KF/natKao without (C3) and with ZB (C4), rPP/KF/comKao without (C5) and with ZB (C6) composites to that of rPP.

Fig. 3 presented the tensile strength of rPP is 21.25 MPa. The rPP/DVB/PP-AA/KF (C2) composites shows that in the presence of 20 phr of KF, the tensile strength can improve to 34.35 MPa (increase 62%). The tensile strengths of rPP/DVB/PP-AA/KF/natKao composites which contained 20 phr of clay without and with 5% ZB addition (C3 and C4) were 38.65 and 39.72 MPa. The tensile strength of C3 and C4 composites compared to that of rPP is 82% and 87%, respectively. When the composite contained 20 phr of comKao with and without 5% ZB addition (C5 and C6) the tensile strengths of composites were 39.18 and 40.33 MPa. TS of C5 and C6 composites compared to that of rPP is 84 and 90%, respectively.

The results of mechanical test composites (C1-C6) of young's modulus (YM), can be seen in Fig. 4. YM of rPP was 144.89 MPa, in the presence of 20 phr of KF can improve the TS of rPP/DVB/PP-AA/KF (C2) composite to 792.46 MPa (increase 447%). The YM of rPP/DVB/PP-AA/KF/natKao composites containing 20 phr of clay without and with 5% ZB addition (C3 and C4) is 1288.23 and 1462.50 MPa. The increase percentages YM of C3 and C4 composites compared to that of rPP is 789 and 909%, respectively. When the composite is added by 20 phr of comKao without and with 5% ZB (C5 and C6) the

YM of composites were 1469.25 and 1575.49 MPa. The increase percentages YM of C5 and C6 composites compared to that of rPP is were 914 and 987% respectively.

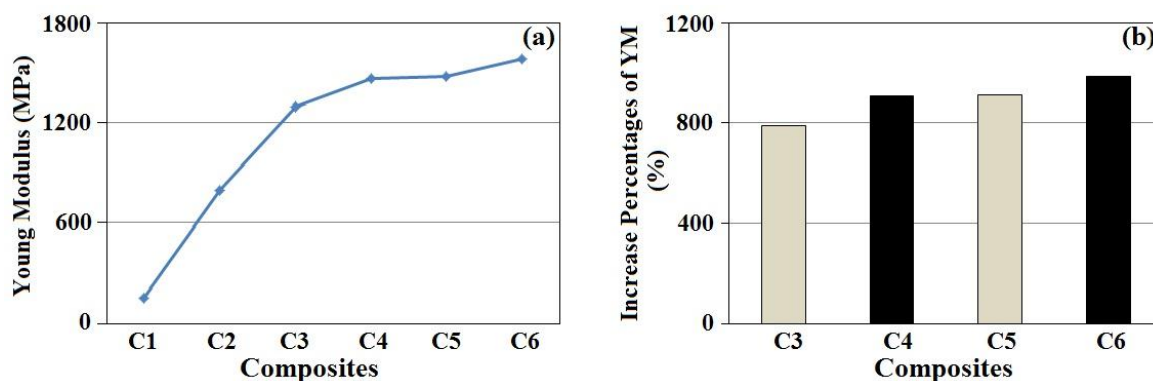


Figure. 4. (a) Young's Modulus (YM) of different composites: rPP (C1), rPP/DVB/PP-AA/KF (C2), rPP/DVB/PP-AA/KF/natKao without (C3) and with ZB (C4), rPP/DVB/PP-AA/KF/comKao without (C5) and with ZB (C6); and (b) YM percentages comparison of rPP/KF/natKao without (C3) and with ZB (C4), rPP/KF/comKao without (C5) and with ZB (C6) composites to that of rPP.

Composite rPP containing 20 phr KF (C2) had improved the mechanical properties, due to the chemical interaction between cellulose and PP, i.e. the formation of carbonyl esters groups as shown from the FTIR spectra (Fig. 1). In the presence kaolin (C3-C6) on the composites interacts by exfoliation (Fig. 2) which can improve the mechanical properties [7,32,33]. The presence of KF and kaolin inside the composites (C3-C6) can form the hydrogen bonding between cellulose and DVB crosslinker as well as kaolin [6,11]. Its caused the mechanical properties increase. The TS of composites containing comKao is was greater than composites containing natKao, due to a lower impurity of comKao. This causes the exfoliate interaction between PP and comKao is more effective [7,32,34]. The addition of 5% ZB in the composite (C4 and C6) can improve the mechanical properties due to a formation of chemical bonding from ZB with the kaolin, Zn-O-Al as shown from the FTIR spectra [28].

Flammability properties

The results of flammability test of composites (C1-C6) of time to ignition can be seen in Fig. 5.

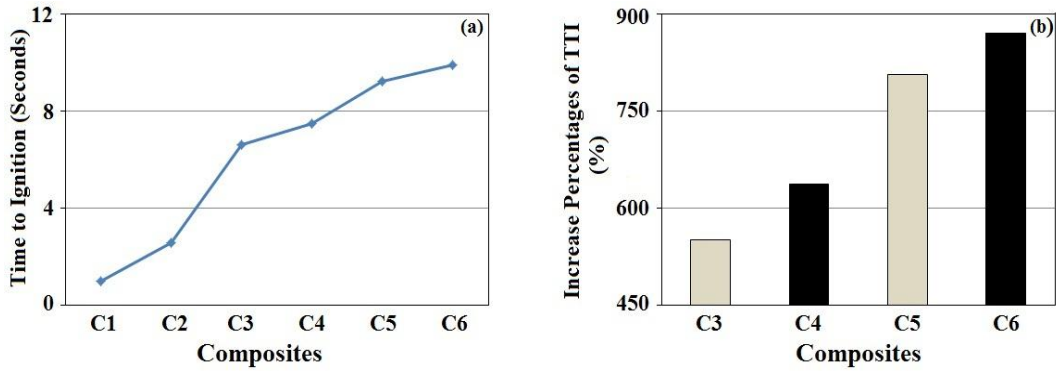


Figure. 5. (a) Time to ignition (TTI) of different composites: rPP (C1), rPP/DVB/PP-AA/KF (C2), rPP/DVB/PP-AA/KF/natKao without (C3) and with ZB (C4), rPP/DVB/PP-AA/KF/comKao without (C5) and with ZB (C6); and (b) TTI percentages comparison of rPP/KF/natKao without (C3) and with ZB (C4), rPP/KF/comKao without (C5) and with ZB (C6) composites to that of rPP.

TTI of rPP was 1.02 s and in the presence of KF (C2) it could inhibit the TTI to 2.61 s (increase 156%). The TTI of rPP/DVB/PP-AA/KF/natKao composites containing 20 phr of kaolin without and with 5% ZB addition (C3 and C4) is 6.64 and 7.51 s. The increase percentages TTI of C3 and C4 composites compared to that of rPP were 551 and 636%, respectively. The composites which added by 20 phr of comKao without and with 5% ZB (C5 and C6) the TTI of composites were 9.24 and 9.89 s. The increase percentages TTI of C5 and C6 composites compared to that of rPP is 806% and 870% respectively. The high TTI of composites reflected good combustion resistance.

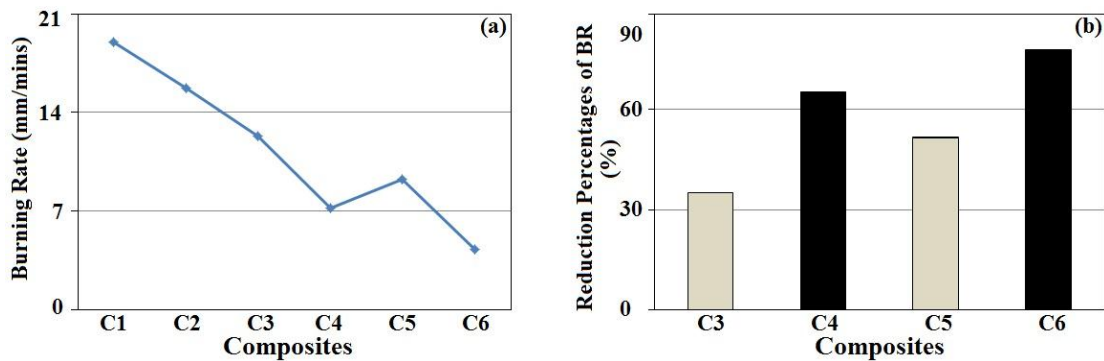


Figure. 6. (a) Burning rate (BR) of different composites: rPP (C1), rPP/DVB/PP-AA/KF (C2), rPP/DVB/PP-AA/KF/natKao without (C3) and with ZB (C4), rPP/DVB/PP-AA/KF/comKao without (C5) and with ZB (C6); and (b) BR percentages comparison of rPP/KF/natKao without (C3) and with ZB (C4), rPP/KF/comKao without (C5) and with ZB (C6) composites to that of rPP.

The results of flammability test composites (C1-C6) of burning rate (BR) can be seen in Fig. 6. BR of rPP was 18.99 mm/min, and in the presence of KF on composites (C2) could slow down the BR to 15.69 mm/min (reduce 17%). This is because the KF has high

thermal stability [20]. The BR of rPP/DVB/PP-AA/KF/natKao composites containing 20 phr of natkaolin without and with 5% ZB (C3 and C4) were 12.32 and 6.62 mm/min. The reduction percentages BR of C3 and C4 composites compared to that of rPP were decreased as 35% and 65% respectively. The BR composite containing 20 phr of comKao without and with 5% ZB addition (C5 and C6) is 9.25 and 4.30 mm/min. The reduction percentages BR of C5 and C6 composites compared to that of rPP is 51 and 77% respectively. The presence of kaolin on composites dispersed well into the rPP then form the exfoliate interaction [31]. This exfoliate interaction of kaolin can improve its inflammability properties of the composites [7,32,33]. ZB fire retardant additive use on burning charcoal can form a stable joint with a layer of silica. During combustion ZB released water and boron oxide, its can inhibit the burning rate [18]. The low BR of composites reflected good combustion resistance.

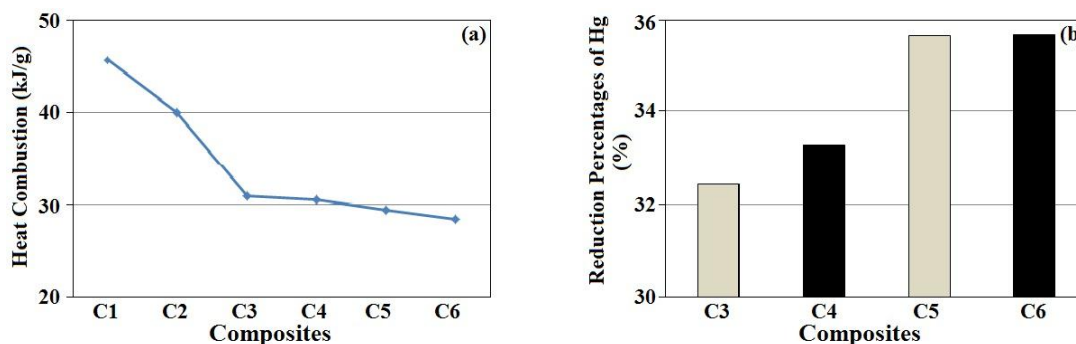


Figure. 7. (a) Combustion (Hg) of different composites: rPP (C1), rPP/DVB/PP-AA/KF (C2), rPP/DVB/PP-AA/KF/natKao without (C3) and with ZB (C4), rPP/DVB/PP-AA/KF/comKao without (C5) and with ZB (C6); and (b) Hg rate percentages comparison of rPP/KF/natKao without (C3) and with ZB (C4), rPP/KF/comKao without (C5) and with ZB (C6) composites to that of rPP.

The heat combustion (Hg) measurement of composites (C1-C6) using a bomb calorimeter is shown in Fig. 7. Hg of rPP was 45.67 kJ/g, the Hg of composites containing 20 phr of natKao without and with 5% ZB addition (C3 and C4) were 30.86 and 30.47 kJ/g. The reduction percentages Hg of C3 and C4 composites compared to that of rPP were 32 and 33%, respectively. The Hg composite containing 20 phr of comKao without and with 5% ZB addition (C5 and C6) is were 29.39 and 28.38 kJ/g. The reduction percentages Hg of C5 and C6 composites compared to that of rPP were 36 and 38%, respectively. This is because the KF that has high thermal stability, and the comKao on burning act as fuel inhibitory due to its carryout endothermic reaction [20]. ZB used on burning can cause charcoal to form a foam inhibits combustion [18]. Compound which having highest

durability fuel was rPP/DVB/PP-AA/KF/comKao+ZB which is was expressed by low heat combustion value.

Conclusion

Different composites formula C3-C6 of rPP/DVB/PP-AA/KF/Kao, with ratio rPP/KF=8/2 (w/w), 20 phr kaolin with and without 5% ZB and 5 phr of ZB had been successfully prepared. It was found that the optimum composite formula was rPP/DVB/PP-AA/KF/comKao+ZB (C6). XRD analysis presented that the kaolin had been exfoliated inside within the PP matrix. Test results of TS and YM showed that the composite rPP/DVB/PP-AA/KF/comKao+ZB is greater than others. The testing results of burning rate (BR) of composites rPP/DVB/PP-AA/KF/comKao+ZB decrease. Based on test results, heat combustion (Hg) of its composites declined. The presence of KF and kaolin on rPP/DVB/PP-AA/KF/comKao+ZB (C6) composite is were able to increase the mechanical properties and also improving combustion resistance.

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- [1] N. S. Suharty, I. P. Almanar, Sudirman, K. Dihadjo, N. Astasari, *Procedia Chemistry*. **2012**, 4, 282-287.
- [2] G. S. Olivares, A. S. Solis, O. Manero, *Int. J. Polym. Mater.* **2008**, 57, 417.
- [3] M. Sarkar, K. Dana, S. Ghatak, A. Banerjee, *B. Mater. Sci.* **2008**, 31(1), 23.
- [4] A. K. Bledzki, A. A. Mamun, O. Faruk, *Express Polym. Lett.* **2007**, 1(11), 755.
- [5] M. Sain, J. Balatinez, S. Law, *J. Appl. Polym. Sci.* **2000**, 77, 260.
- [6] H. S. Yang, H. J. Kim, H. J. Park, B. J. Lee, T. S. Hwang, *Compos. Struct.* **2007**, 77, 45.
- [7] E. Moncada, R. Quijada, I. Lieberwirth, M. Yazdani-Pedram, *Macromol. Chem. Physic.* **2006**, 207, 1376.
- [8] R. Anjana, K. E. George, *IJERA* **2012**, 2(4), 868-872.
- [9] R. T. Woodhamd, G. Thomas, D. K. Rodgers, *Polym. Eng. Sci.* **1984**, 24(15), 1166.
- [10] H. S. Kim, H. S. Yang, H. J. Kim, *J. Appl. Poly. Sci.* **2005**, 97, 1513.
- [11] N. S. Suharty, B. Wirjosentono, M. Firdaus, D. S. Handayani, J. Sholikhah, Y. A. Maharani, *J. Phys. Sci.* **2008**, 19, 105.
- [12] J. O. Metzger, M. Eissen, *Comptes Rendus Chimie.* **2004**, 7, 1.
- [13] H. G. B. Premalal, H. Ismail, A. Baharin, *Polym Test.* **2002**, 21, 833.
- [14] N. S. Suharty, M. Firdaus, Proceeding of 12th Asian Chemical Congress, Kuala Lumpur, Malaysia, 2006.
- [15] S. Sinha Ray, Y. Kazunobu, O. Masami, F. Youhei, O. Akinobu, U. Kazue, *Polymer.* **2003**, 44, 6633.
- [16] P. Pasbakhsh, H. Ismail, M. N. Ahmad Fauzi, A. Abu Bakar, *Polym. Test.* **2009**, 28, 548.
- [17] J. W. Gilman, C. L. Jackson, A. B. Morgan, R. H. Harris, *Chem. Mater.* **2000**, 12, 1866.
- [18] P. K. Patra, S. B. Warner, Y. K. Kim, Q. Fan, P. D. Calvert, S. Adanur, NTC Annual Report. No. M02-MD08, **2005**, 1-10.
- [19] I. Sobolov, E.A. Woycheshin, in: "Handbook of fillers for plastics", H.S.Katz, J. Milewski, Eds., Van

- Norstrand Reinhold, New York 1987, 292.
- [20] G. Tesoro, *J. Polym. Sci: Macromol. Rev.* **1978**, 13, 283.
 - [21] Z. Al Hassany, A. Genovese, R. A. Shanks, *express Polym. Lett.* **2010**, 4(2), 79.
 - [22] H. Ismail, R. Nordin, Z. Ahmad, A. Rashid, *Iran. Polym. J.* **2010**, 19(4), 297.
 - [23] H. Ismail, M. R. Edyham, B. Wirjosentono, *Polym. Test.* **2002**, 21, 139.
 - [24] S. Al-Malaika, N. S. Suharty, *Polym. Degrad. Stabil.* **1995**, 49, 77.
 - [25] B. R. Ilic, A. A. Mitrovic, L. R. Ljiljana, *Hem. Ind.* **2010**, 64(4), 351.
 - [26] R. M. Silverstein, C. Bassler, T. C. Morrill, “Spectrometric Identification of Organic Compounds”, John Wiley and Sons Inc, New York 2005, p.83.
 - [27] L. Vaculikova, E. Plekova, S. Vallova, I. Koutnik, *Acta Geodyn. Geomater.* **2011**, 8(1), 59.
 - [28] Roto, T. Iqmal N. S. Umi, *Indo. J. Chem.* **2008**, 8(3), 307.
 - [29] N. Tugrul, B. A. Nil, *Internt. Conf. Chem. and Chem. Process.* **2011**, 55.
 - [30] J. E. Gardoli nski, P. P. Zamora, F. Wypych, *J. Colloid. Interf. Sci.* **1999**, 211, 137.
 - [31] T. P. Mohan, M. R. Kumar, R. Velmurugan, *J. Mater. Sci.* **2006**, 41, 2929.
 - [32] Kusmono, Z. A. M. Ishak, W. S. Chow, T. Takaechi, Rochmadi, *express Polym. Lett.* **2008**, 2 (9), 655.
 - [33] M. A. HaiYun, S. PingAn, F. ZhengPing, *Sci. China. Chem.* **2011**, 41(2), 314.
 - [34] Q. Zhang, Q. Liu, J. E. Mark, I. Noda, *Appl. Clay Sci.* **2009**, 46, 51.