Properties of Wood Plastic Composite Using Primary Sludge as Filler

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Abstract

Sludge is the largest waste produced from the pulp and paper mill, it consists of 50-60% fibers and inorganic materials and have caused serious disposal problem. Recycling sludge into value-added product can give environmental and economic benefits. The objective f this research was to optimize utilization of sludge as filler in wood plastic composite using polypropylene as a matrix resin. Sludge with and without purification treatment were used as filler. The concentration of filler used was 40%, 50% and 60%. Maleic anhydride-modified- polypropylene (MAPP) with concentration of 5% was used as a coupling agent. Filler, matrix with and without coupling agent were compounded using Haake polydrive labopastomill at 175 °C, 60 rpm for 20 min. The results indicated that the morphology, physical, mechanical and thermal properties of wood plastic composites was much influenced by purification treatment, filler loadings and addition of coupling agent. Interaction of between fibers and matrix resin and thermal stability of wood plastic composites were much improved by purification treatment on sludge and addition of coupling agent.

Keywords: coupling agent, fillers, purification, sludge, wood plastic composite

Abstrak

Sludge adalah limbah terbesar yang dihasilkan dari pabrik pulp dan kertas, terdiri dari 50-60% serat dan bahan anorganik. Penanganan *sludge* menyebabkan masalah terutama dalam hal pembuangannya. Daur ulang *sludge* menjadi produk yang memiliki nilai tambah dapat memberikan manfaat lingkungan dan ekonomi. Penelitian ini bertujuan untuk memanfaatkan secara optimal *sludge* sebagai pengisi dalam pembuatan komposit kayu plastik dengan matrik polipropilena. *Sludge* dengan dan tanpa perlakuan purifikasi digunakan sebagai pengisi. Konsentrasi pengisi digunaka sebanyak 40%, 50% dan 60%. *Maleic anhydride-modified-polypropylene* (MAPP) dengan konsentrasi 5% digunakan sebagai agen pengkopel. Pengisi, matrik dengan dan tanpa agen pengkopel dicampur menggunakan Haake polydrive labopastomill pada suhu 175 °C dengan laju putaran 60 rpm selama 20 menit. Hasil penelitian menunjukkan sifat morfologi, sifat fisis, mekanis dan termal komposit kayu plastik dipengaruhi oleh perlakuan purifikasi, kadar pengisi dan pemberian agen pengkopel. Perlakuan purifikasi dan penambahan agen pengkopel terutama mempengaruhi interaksi antara serat dan matriks polipropilena serta meningkatkan stabilitas termal dari komposit kayu plastik.

Kata kunci: agen pengkopel, komposit kayu plastik, pengisi, purifikasi, *sludge*

Introduction

Natural fiber has been widely used as the primary material in the manufacturing of plastic composite for its advantages over synthetic fiber. Other than plant's waste, the sludge from pulp and paper industry also acts as a potential source of cellulose. Sludge consists of fiber (50-60%) and inorganic materials such as mineral and ash (Mehmood *et al.* 2010), thus it has the potential to be utilized as an alternative source of cellulose. However, as natural fiber, sludge has its disadvantages, such as the existence of hydroxyl groups and other polar groups which are causing it to have hydrophilic properties which can resulted in low wettability and poor interface bonding with matrix resin (Taramian *et al.* 2007, Li *et al.* 2011, Lima *et al.* 2014). The poor bonds between hydrophilic fiber and hydrophobic matrix could affect the physical and mechanical properties of the composites product. Faruk *et al.* (2012) explained that in order to increase the interface adhesion between the fiber and the matrix, there should be a modification in the matrix or the fibers.

The modification of fiber can be conducted through physical and chemical methods, in which the physical methods such as corona/plasma and mercerisation aim to affect the mechanical bonding with polymer matrix. Moreover, the chemical modification of fiber aims to form the hydroxyl group reaction in fiber with correct reactive compound in order to form covalent bonding. The newly formed group will act as the interface between the fiber and the matrix to produce composite products with better properties. The use of third component besides the matrix and fiber is also categorized as chemical method, known as compatibilizer, or coupling agent. The coupling agent's function is modifying one or both of the two component of the composite in order to improve its adhesion (Lu *et al.* 2000, Febrianto *et al.*2005, 2006a, 2006b, 2006c, 2014).

Examples of coupling agents that have been used in several researches are maleic anhydride polypropylene (MAPP), maleic anhydride polyethylene (MAPE), isocyanate, silane, and other anhydride such as acid and succinic anhydride (Lu *et al.* 2000, Febrianto *et al.* 2005, Febrianto *et al.* 2006a, 2006b). MAPP and MAPE are obtained through the reaction between the matrix and MAH with additional initiator. The coupling agent widely used in the manufacturing of plastic composite with PP matrix is MAPP. Maleic anhydride has advantages such as its effectivity in low concentration, low surface energy, can be obtained commercially, and not require pretreatment of the fiber or PP before its manufacturing (Lu *et al.* 2000; Lin *et al.* 2002; Kim *et al.* 2007). This research aims to determine the effect of MAPP towards the mechanial and thermal properties of the manufactured plastic composite.

Materials and Methods

Materials used in this research are primary sludge obtained from PT. Indah Kiat Pulp and Paper, Serang-Banten. Polypropylene impact copolymer (block copolymer) BI9.0GA was obtained from PT. Chandra Asri Petrochemical, Cilegon. The most important characteristics of PP impact copolymer (block copolymer) BI9.0GA is its impact-resistance material (it's hard to break) and its resistance of low temperature (reaching as low as -30 ºC), melt flow rate (MFR) of 9.0 g per 10 min., and its density of 0.9 g cm^{-3}. The coupling agent used is Licocene PPMA 6452 TP, produced by Clariant

Chemical, Ltd., Germany. Several characteristics of Licocene PPMA 6452 TP are its acidic number of 41 mg KOH/g, its softening point of 143 ºC, its density of 0.93 g cm^{-3}, and its grafting level of maleic anhydride (7%). The chemical materials used are ethanol, benzene, sodium chloride (NaClO$_2$), acetic acid, sodium hydroxyde, destilated water, and acid chloride.

Purification treatment

The purification treatment was conducted in order to isolate the cellulose component of the primary sludge, and it was based on the methods of Fahma *et al.* (2010). Firstly, sludge was extracted using ethanol/benzene solution (1:2 v/v) through soxhlet extraction for 48 h to remove the extractive components (resin, oil, fat, and wax). Further, fiber was washed using ethanol to remove the benzene, followed by rinsing using destilated water. Afterwards, bleaching was conducted using sodium chloride solution 1.25% in acidic condition (pH = 4-5). Bleaching treatment was conducted at 70 °C for 4 h. Fiber was rinsing with destilated water until pH 7. Furthermore, fiber was extracted with sodium hydroxyde 17.5% for 2 h at 20 °C, and rinsing several times with destilated water to remove the alkali. Finally, the fiber was extracted with 1M acid chloride solution to remove the inorganic materials. Fiber was rinsing with destilated water until pH 7, and then it was dried at 50 °C.

Plastic composite manufacture

The composite was manufactured through the following steps: the mixing of sludge, PP matrix, and MAPP using Haake Polydrive labo plastomill at 175 °C and 60 rpm for 20 min. The composition (percentage) of materials used by sludge/PP/MAPP are 40/55/5, 50/45/5, and 60/35/5. Afterwards, the resulting mixture was formed into pellets, and then manufactured into sheets/composites using hot press at 180 °C for 20 min. Further, it was cold-pressed for 10 min. After, the manufactured composite was conditioned at room temperature and cutting into specific sizes to be examined.

Plastic composite characterizations

The physical properties of composite film consist of water absorption and thickness swelling with the samples' size of (2×2) cm^2. Before the testing, each samples' mass and thickness were measured. After, samples were soaked in aquades at room temperature for two days. After two days, each samples were swabbed using tissue paper to wipe off the water and then their mass and thickness were determined. The examination of mechanical properties (tensile strength, young modulus, and break elongation) of composite film was conducted based on ASTM D882-75b (Standard Test Method for Tensile Properties of Thin Plastic Sheeting) with the crosshead speed of 50 mm/min. The sludge-filled composite's morphology was analyzed using SEM (Scanning Electron Microscope) JEOL-JSM 6510LV. In this morpology analysis, samples were put down on the carbontape fixed to the samples holder of 1 cm diameter. Samples were coated with osmium in coating device, and then they were put into SEM and scanned with the voltage of 15 kV. The thermal properties of composite were determined using TGA (Thermo-Gravimetrix Analysis) and DSC (Differential Scanning Calorimetry). The TGA testing was conducted by taking 10 mg of the composite samples and then put into the

crucible. This samples-contained crucible was placed inside a testing chamber with heating program at 50 °C to 600 °C and rising temperature speed of 10 °C min⁻¹ and nitrogen gas flow speed of 50 ml min⁻¹. Afterwards, it was put into hold (isothermic) for 5 minutes at 600 °C before the heating was continued again until it reached 900 °C in the oxygen gas-environment and oxygen gas flow speed of 50 mL/min. The DSC testing was conducted using DSC Mettler Toledo type-DSC 821. 16 mg of samples were then put into the 40 µL crucible. The analysis was conducted with temperature program from -75 to 125 ºC with heating speed of 5 ºC min⁻¹. The purging gas used was nitrogen with flow speed of 50 ml min⁻¹.

Results and Discussion

Physical and mechanical properties of plastic composite

Figure 1 shows the density of composite. The increasing fiber content added into the PP matrix tends to increase the density. The addition of MAPP toward all treatments also causing the increasing of composite's density, due to the interaction between PP with sludge becomes better and thus decrease the amount of empty spaces/gaps between the fibers and matrix.

Figure 2 shows the water absorption properties and thickness swelling tendency of the composite after two days being submerged. The water absorption in all treatments increases with the increasing amount of fiber. The natural properties of plastic matrix is hydrophobic, which means the water was absorbed by cellulose materials inside the composite (Hamzeh et al. 2011). The decrease of water absorbed was caused by the addition of MAPP in all of the treatments. The addition of MAPP was probably causing the forming of better linkages between matrix and fiber, for it decreases the amount of gaps on the composite's interface. Moreover, the fiber's hydrophilic properties was blocked by the existence of hydroxyl group, due to the coupling agents increase the amount of ester bonds between hydroxyl group in the fiber with the anhydride group in MAPP.

Our result was agreed with the previous result reported by Febrianto et al. (2006a) using woody filler in manufacturing wood flour-poly lactic acid composites.
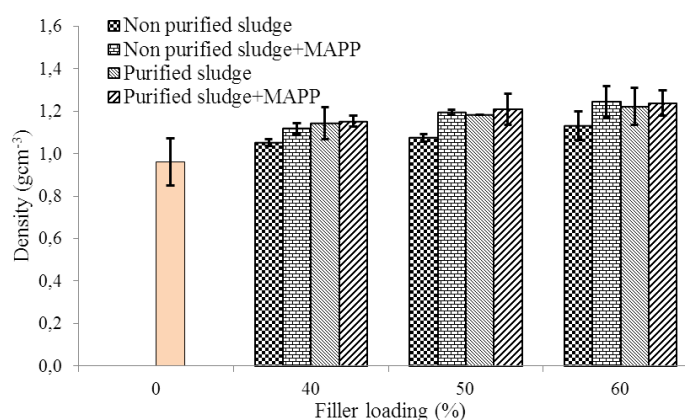

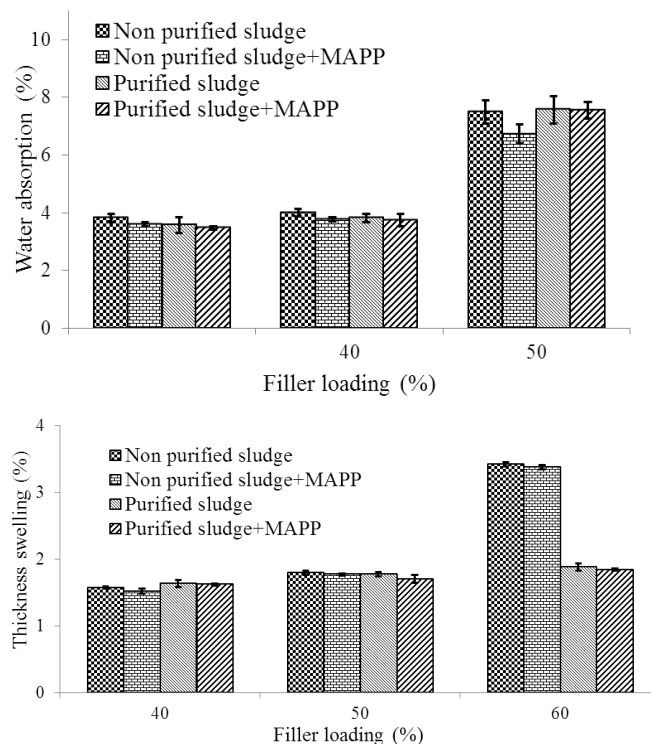Figure 1 The density of the plastic composite.

Figure 2 Water absorption and thickness swelling of the composite.

The thickness swelling properties of the composite show the same tendency with the water absorption properties. The hydrophilic properties of lignocellulosic materials are mostly caused by the existence of polar groups which pull the water molecules by hydrogen bond. This causes the water molecules trapped within fiber cell's wall (causing the cells to swell) and also in the interfaces between fiber and the matrix. This affects the dimensional changes of plastic composite, especially on its thickness (Hamzeh *et al.* 2011). Figure 3 shows the results of tensile strength testing of sludge-filled plastic composite. The tensile strength decreases by the increasing of amount of fiber of the composite. These decreases are caused by the heterogenity of sludge's size, due to the composites are not able to withstand the stress transferred from the matrix to the filler.

Similar result was reported by Febrianto *et al.* (2005) increasing the filler loadings resulted in decreasing the tensile strength and breaking elongation and increasing the Young's modulus of wood polypropylene composite.

The addition of MAPP towards all composites increases their tensile strength. This increase in strength occurred because of the better bonding between fiber and PP. The increase in interaction between fiber and PP happens through esterification between anhydride groups of MAPP with hyrdroxyl groups of fibers. Figure 4 shows the mechanism of chemical reaction in the forming of interface bonding between fiber's surface with matrix. The reaction begins through

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the peroxyde catalyst which starts the forming of radical on PP chain through hydrogen bonding and chain breaking. The formed radical further reacts with maleic anhydride to form MAPP (Park *et al.* 2006, Febrianto *et al.* 2005).

Figure 5 shows that there is an increase in young modulus of the plastic composite along with the increase of sludge content. Young modulus shows the composite's rigidity. The larger the amount of fiber added into the matrix, the composite structure becomes more rigid. The addition of MAPP increases the composite's rigidity for there is a compatibility between the fiber and the matrix. Figure 6 shows the break elongation graphic of the composite, in which the addition of fiber causes the composite to become more rigid and its break elongation to decline.
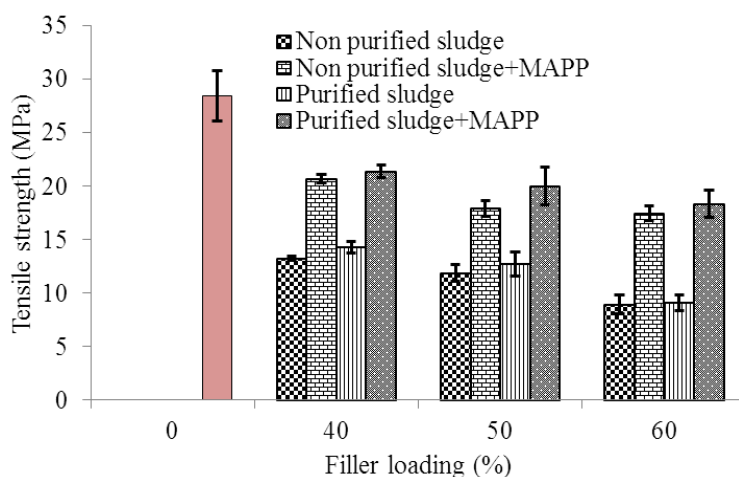

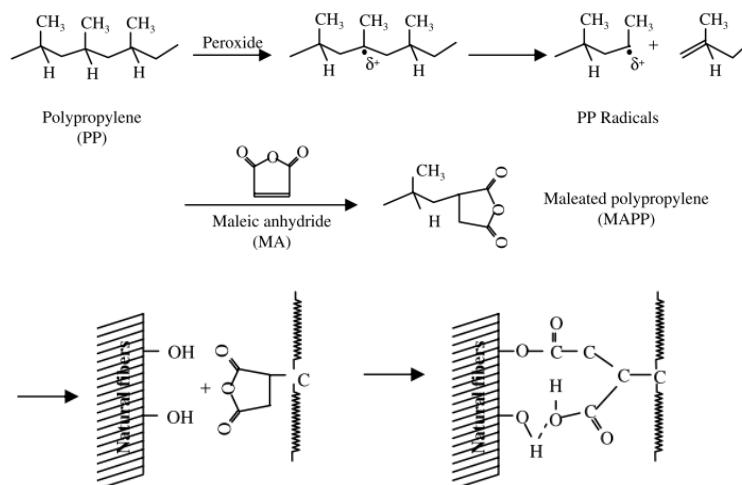Figure 3 Tensile strength of plastic composite.

Figure 4 The mechanism of chemical reaction between fiber with MAPP.
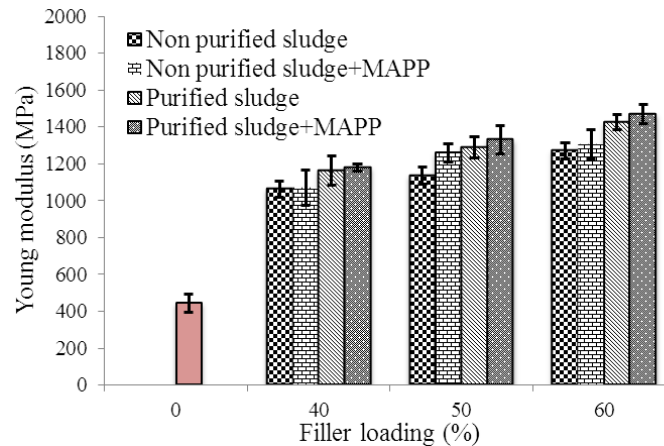
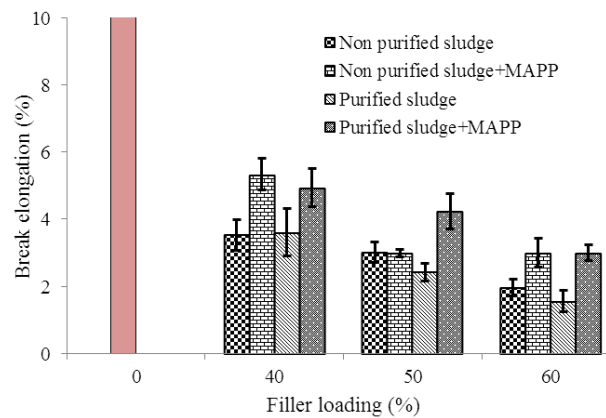Figure 5 Young modulus of plastic composite.

Figure 6 Break elongation of the plastic composite.

Figure 7 shows the SEM results of the composite with PP matrix based on the varied sludge treatment. There are morphological differences of the composite's surface made with the different fillers and sludge treatments. The unpurified sludge-filled composite shows the existence of gaps between fibers and matrix which indicates that the interaction between fiber and the matrix does not occured. While the composite added coupling agents already seen the interaction between the fibers with the matrix has shown by the matrix that surrounds the fiber so it is not seen again the gap between the fibers with the matrix. The similar thing also occured on the purified sludge-filled composite.

Thermal properties of plastic composite

Figure 8 shows the TGA thermogram of sludge, PP film composite, and PP film composite with sludge filler. The steps of sludge's mass declination from the heat was started with the change of mass caused by water evaporation from the fiber at 50-150 °C (Figure 8a). The next step is the mass change caused by initial damage of sludge at 200-350 °C.

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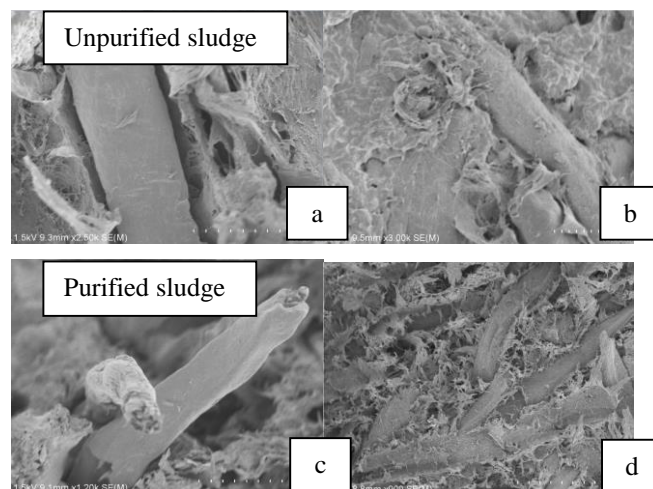
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Figure 7 SEM image of plastic composite filled: a) unpurified sludge without MAPP, b) unpurified sludge with MAPP, c) purified sludge without MAPP, and d) purified sludge with MAPP.

According to Onggo *et al.* (2005), in this step, the components inside the fiber undergo carbon chain breaking, followed by the secretion of volatile matters such as carbon dioxide, hydrocarbon, and hydrogen gas. Components with lower molecular mass will undergo degradation before the components with high molecular mass. Therefore, on fiber, the degradation is firstly experienced by hemicellulosic component, lignin, and lastly, cellulose which produces charcoal. Further, the mass change was happened because of the oxydation reaction of residue such as charchoal, followed by the process of carbon burning into ashes which happened at 400-600 °C.

PP decomposition shows one degradation step with the mass diminution on the exothermic peak at 420 °C (Figure 8b). Moreover, on composite with 50% PP-50% sludge, the decomposition consists of two steps of mass reduction. The first step is caused by the sludge and PP: the amalgamation of 50% sludge in PP matrix increases the

sludge component decomposition at 320 °C (sludge decomposition at 300 °C). This shows that PP is the component protecting the fibers, thus delaying the degradation. The second step is the consistent decomposition of PP at ≈420 °C, showing that the existence of sludge doesn't affect the thermal stabilization or mass reduction of the matrix greatly (Spoljaric *et al.* 2009).

For the composite film with 45% PP-5% MAPP-50% sludge (Figure 8d), the observed changes in decomposition profile is the change in mass reduction steps according to the matrix. The decomposition temperature of the matrix increases toward 440ºC. The rate of mass reduction slightly decreases compared to the composite without coupling agent. This change is caused by the existence of coupling agent inside the composite. The specific interaction between cellulose and maleat anhydride could produce an association through esterification between anhydride group and hydroxyl group of the cellulose (Spoljaric *et al.* 2009).
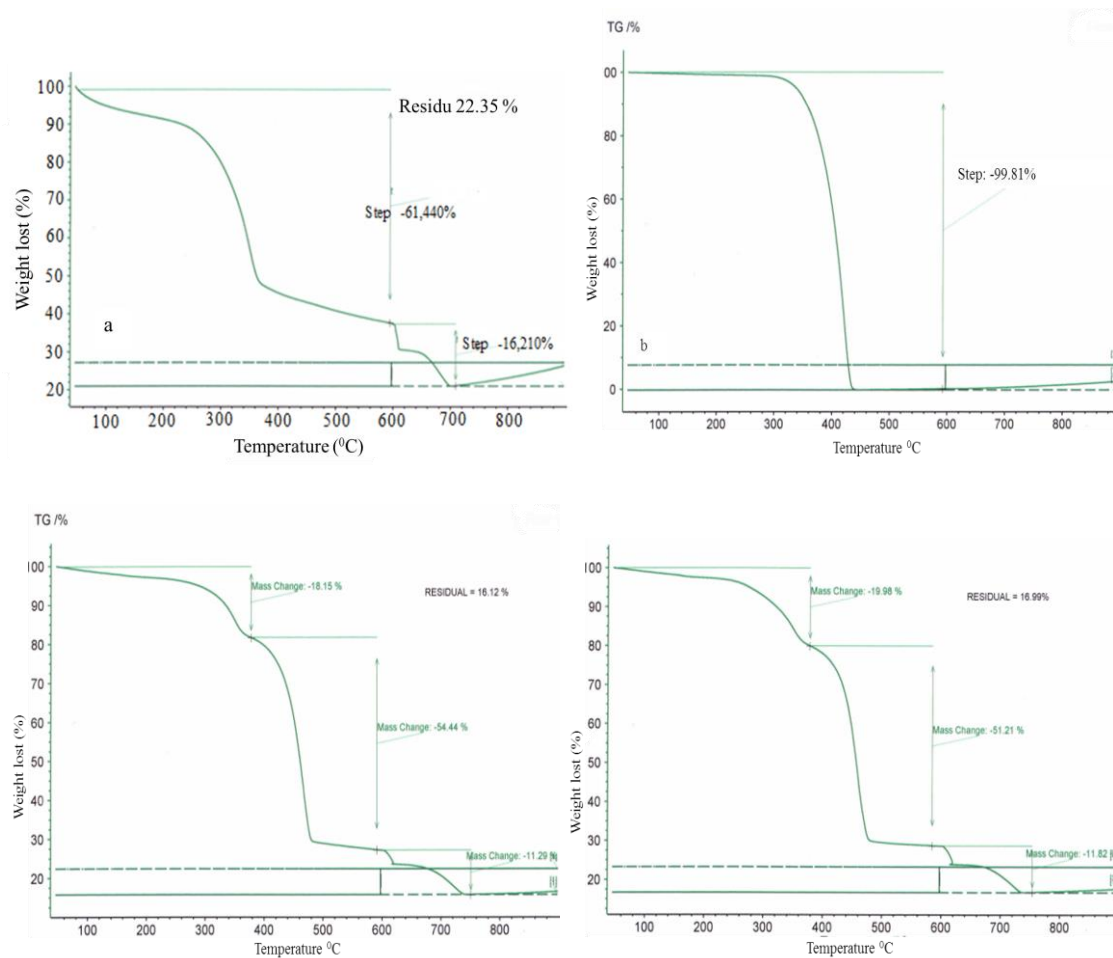
Gambar 8 TGA thermogram on a) sludge; b) PP composite film; c) composite film with 50% sludge-50% PP and d) composite film with 50% sludge-45% PP-5% MAPP.

Figure 9 shows the DSC thermogram of the composite to determine the glass transition temperature and melting point of the manufactured composite. The first endothermic peak of PP film (115 °C) is the process of the increasing of glass transition at 125 °C in the PP composite with sludge filling, whereas on the PP-sludge composite with MAPP addition, the glass transition temperature is the same as the PP's. The second endothermic of the PP film (163.73 °C) shows the process of polymer meltdown from its solid state into liquid. The addition of sludge toward matrix causes the melting point to increase at 164.40 °C. However, the addition of MAPP on the PP-sludge composite decreased the melting point into 160.38°C. The ΔH value is the change of calor which was happening along the calor absorption or desorption process, showing that the addition of MAPP toward the composite causes the change of calor becoming smaller.

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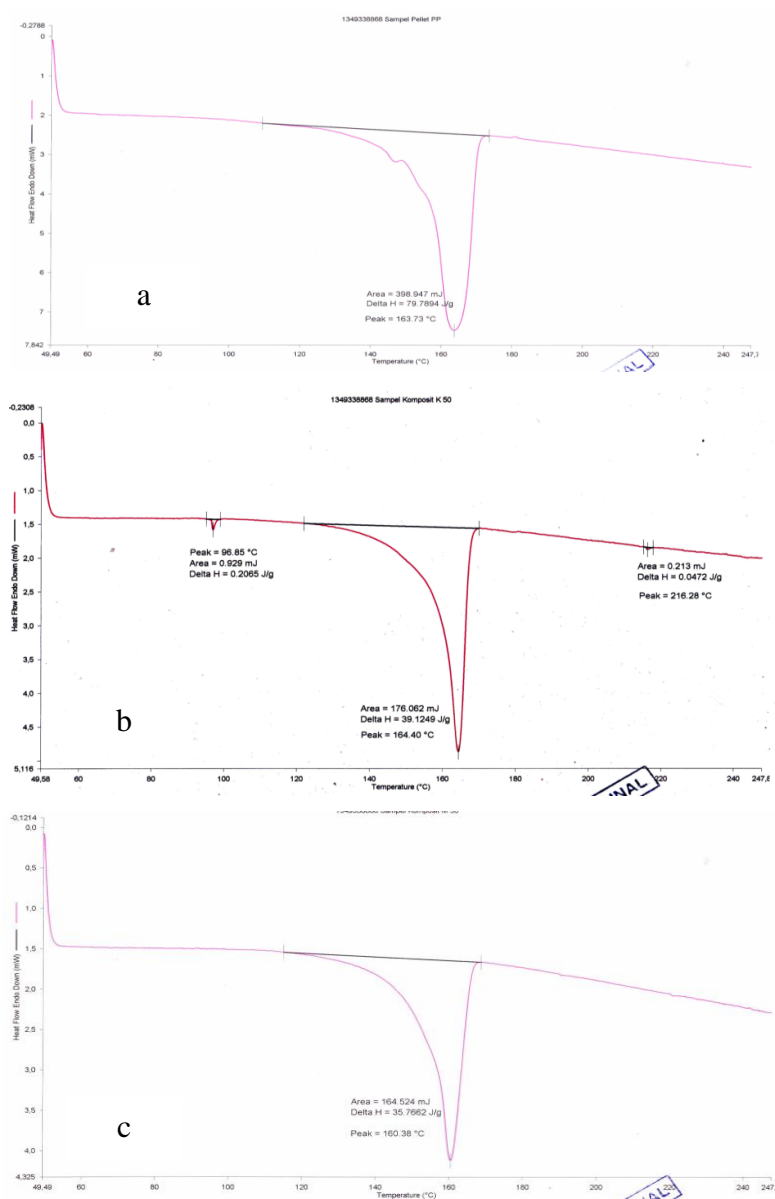
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Figure 9 DSC thermogram of a) sludge; b) PP composite film; c) composite film of sludge 50%-PP 50% and d) composite film of sludge 50%-PP 45%-MAPP 5%.

Table 1 Thermal characteristics of composite

Sample	Glass transition (^{0}C)	Melting point (^{0}C)	ΔH (J/g)
PP (pure)	115	163.73	79.7894
Sludge Composite 50%-PP 50%	125	164.40	39.1249
Sludge Composite 50%-PP 45%-MAPP 5%	115	160.38	35.7662

Conclusion

Purification treatment of sludge prior to be used as filler improved the physical, mechanical and thermal properties of wood plastic composites. The physical and mechanical properties of wood plastic composites were also influence by filler loadings. The addition of coupling agents improved the interaction between the fiber and the matrix in the manufacturing of wood plastic composite. The SEM results of the composite added with coupling agent show good interaction between the fiber and the matrix, as was shown by the matrix which engulfs the fiber, leaving no gaps between the fibers and the matrix. The addition of coupling agent also improved the thermal stability of the manufactured composite, as is shown by the increase of temperature of matrix decomposition, mass loss rate, and the decrease of the calor's change.

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