SOLID WASTE-SILICA COMPOSITE FOR HIGH STRENGTH AND LIGHTWEIGHT MATERIAL APPLICATION

KOMPOSIT SAMPAH-SILIKA UNTUK APLIKASI MATERIAL KUAT DAN RINGAN

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ABSTRAK

Komposit sampah sudah berhasil dibuat. Mula-mula, komposit disintesis dengan menggunakan poliuretan sebagai pengikat yang dicampur dengan sampah melalui metode pencamnpuran sederhana (simple mixing), kemudian dihot-press pada tekanan 4 metric ton dan suhu 100⁰C selama 20 menit. Untuk meningkatkan kekuatan mekaniknya, nanopartikel silica dengan berbagai komposisi ditambahkan dalam campuran poliuretan-sampah. Dengan menggunakan uji kekuatan tekan, didapatkan komposit poliuretan-sampah dengan fraksi volume sampah sebesar 87,15% memiliki kekuatan tekan sebesar 160 MPa. Selanjutnya, dengan penambahan silica sebesar 0,4975% (v/v) kekuatan tekan komposit menjadi 200 MPa, atau meningkat sebesar 23% dibandingkan komposit tanpa silica. Peningkatan ini juga dikonfirmasi melalui FTIR Spectroscopy yang menunjukkan adanya pergeseran kecil pada puncak spektra poliuretan akibat penambahan silica, utamanya pada gugus fungsi amina dan karbonil. Kekuatan mekanik komposit ini lebih baik daripada batu bata (80 MPa), batuan shale (73 MPa), batuan siltstone (92 MPa) dan beberapa jenis batuan yang lain. Dengan menggunakan uji kerapatan didapatkan komposit ini memiliki massa jenis 0,7 g/cm3, setara dengan kayu Jati (Tectona grandis) dan Mahoni (Swietenia macrophylla) yang memiliki massa jenis masing-masing 0,8 g/cm3 dan 0,7 g/cm3. Ini menunjukkan komposit yang dihasilkan sangat cocok untuk diaplikasikan sebagai bahan bangunan pengganti kayu.

ABSTRACT

The solid waste composite was successfully made. Preliminary, the composite was synthesized using polyurethane as binder mixed with the solid waste using simple mixing method and then hot-pressed at at pressure of 4 metric-tons and temperature of 100⁰C for 20 minutes. To enhance its strength, silica nanoparticles with varied content then were added in the polyurethane-solid waste mixture. From the compressive strength test, it was obtained that polyurethane-solid waste composite with solid waste volume fraction of 87.15% had optimum compressive strength of 160 MPa. Meanwhile, for silica addition with the fraction of 0.4975%, the compressive strength became 200 MPa, or increased 23% of that without nanosilica. The enhancement was also briefly confirmed from FTIR Spectroscopy where some polyurethane spectra shifted small due to silica addition, especially in amine and carbonyl groups as its active groups. The strength is better than of brick (80 MPa), shalestone (73 MPa), silstone (92 MPa) and other stones. From density measurement, the composite-produced has density about 0.7 g/cm3 that comparable to Jati (Tectona grandis) and Mahoni (Swietenia macrophylla) having densities about 0.8 g/cm3 and 0.7 g/cm3 respectively. Therefore, this composite is very adequate for building material application to compete the woods.

INTRODUCTION

The issue of solid waste growth is a serious problem for several cities especially in developing countries. Additionally, per capita production of the solid waste is about 2.5 to 3 liters per day (Masturi et al, 2011), that is greater than its decomposition and reutilization. Therefore, some innovative and creative efforts for handling the rapid growth absolutely are extremely important and urgent, and one of them that can be done to solve the serious growth waste is recycling the waste to composite material competing the woods. Beside as a

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solution of solid waste accumulation problem, it also contributes in reducing deforestation.

Some research related to solid waste composite have been done, such as leaves composite using epoxy resin matrix and silica reinforcement (Hadiyawarman et al, 2008), leaves and paper waste composite with compressive strength of 85 MPa using polyvinyl acetate polymer as binder and silica nanoparticle as reinforcement (Masturi et al, 2011) and agriculture waste composite using silica nanoparticle filler without binder with compressive strength of 57 Mpa (Kumagai & Sasaki, 2009). Even though the strength-produced has been comparable to some stones or concretes, however, the strength may enable to be improved to obtain the composite with higher strength and one of the ways is making solid waste composite using other polymer as binder with stronger binding.

In this work, it was performed the utilizing of leaves and paper waste using polyurethane (PU) as binder and nanosilica as reinforcement. PU was chosen as matrix because of its excellent binding strength and has been used in several composites such as composite using cellulose fibers (Maafi et al, 2010), interlayer fiber composite (Lavorgna et al, 2007), organoclay composite for automotive application (Khudyakov et al, 2009) and silica nanocomposite for coating application (Türünç et al, 2008), meanwhile, silica nanoparticle was also used as reinforcement because of its mechanical properties, moreover its size is in nanometer its interaction to the matrix and the solid waste will be stronger due to increasing of the interaction area (Gan, 2009).

The aim of this work is to obtain a solid waste composite having very high strength, lightweight and low-cost in the production so it will enable to be used as building materials to compete the woods. This paper briefly described the compressive strength of the solid waste composite using polyurethane as matrix and nanosilica as reinforcement.

METHODS

The materials are solid waste consisting of dry leaves and paper with composition 1:1, polyol and diisocyanate (polyurethane raw materials) and silica nanoparticles purchased from Brataco Chemical, Inc. (Indonesia).

Leaves and paper waste was crushed separately using blender machine, while diisocyanate and polyol were mixed to form poly-

urethane, and then mixed in the 6 mL of aquades by stirring using magnetic stirrer machine for 15 minutes. The leaves and paper-crushed then were put into PU-water mixture and stirred until became homogenous to be hot-pressed at 4 metric ton and 80°C of pressure and temperature respectively for 20 minutes. The sample then was put off the mould to be dried into oven machine at 80°C of temperature for one hour. In this work, the composition of PU and solid waste was varied to obtain composite with maximum compressive strength where called as optimum composition or fraction. Finally, into the optimum composition, silica nanoparticles were added variously to obtain maximum improvement of the compressive strength. The samples-produced had diameter 5 cm and the thickness varied from 15 mm to 20 mm depending on the materials (solid waste, PU and nanosilica) composition, temperature and pressure of hot-press.

The compressive strength as main characterization was measured. Prior to be tested, sample was cut to be cubic-form according to ASTM standard (ASTM C0109M-02) and contact area varied from 225 mm^2 and 400 mm^2 depending on the sample thickness. The test was done using Torsee Tokyo Testing Machine MFG Ltd. equipped with Load Cell. The van der Waals interaction and bonding measurement, especially between polymer (PU) and silica were recorded using FTIR Spectrometer Shimadzu Prestige 21. The average size of silica was measured using SEM Analytical Scanning Microscope JEOL JSM 6510 LA. Finally, the density measurement of PU, solid waste and composite-produced was performed by measuring its mass and geometrical size using Ohauss Adventurer ISL AS153 and Tricle Brand respectively.

RESULTS AND DISCUSSION

In this work, polyurethane (PU) was prepared by polyol and diisocyanate sol gel polymerization with weight composition of 5 : 1 (Isnaneni et al, 2013; Masturi et al, 2016), while the density of solid waste (in pressed condition), nanosilica and PU was obtained about 0.902 g/cm^3, 2.648 g/cm^3 and 1.530 g/cm^3 respectively to obtain their volume fraction (Fig. 1). The effect of polyurethane addition into the solid waste particles can be explained in the term of the improvement of interaction area. Even though pressed under high pressure, prior to polyurethane presence as a binder the pristine

solid waste still have many pores corresponding to brittleness of the composite. The presence of PU is to fulfill the pores so the interaction area improves. In addition, the polymer without filler has low mechanical strength and stiffness because its chains are still pliable and free to move. Having added solid waste particles, polymer chains become stiffer and as a result the composite strength increase too.
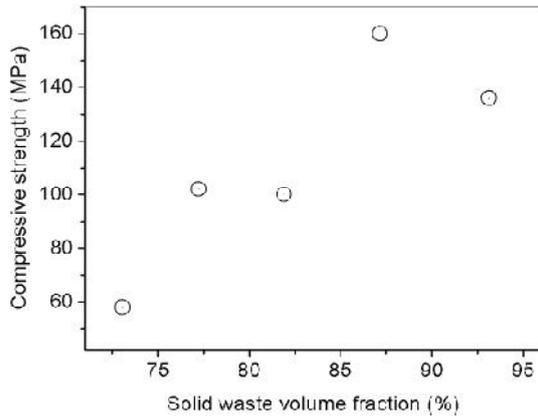

Figure 1. The compressive strength as function of solid waste volume fraction (%vol). Maximum strength of 160 MPa was observed for solid waste fraction of 87.15%vol.

The occurrence of maximum compressive strength due to solid waste presence (Fig. 1) can be understood as result of the appearance of contacts between particle surfaces and PU [10]. As fraction of solid waste increases, the compressive strength increases too, however, at higher fraction of solid waste, contacts between particles causing brittleness appear and absolutely reduce the fraction of contacts between particle and polymer. As a result, the compressive strength decreases. In this work, the optimum volume fraction of solid waste is 87.15% with compressive strength obtained was 160 MPa.

To enhance further the compressive strength, nanosilica was added into the optimum fraction above. Figure 3 shoews SEM image of silica demonstrated that the particles are spherical shape with the average diameter is 74 nm (Masturi et al, 2011(b)). As its excellent mechanical strength, the addition of nanosilica affects to the composite compressive strength improvement (Gan *et al*, 2008). As the fraction of nanosilica increases, the compressive tends to increase until its optimum fraction. The addition of nanosilica above the optimum fraction reduces the compressive strength-produced as result of appearance of interfacial or contact
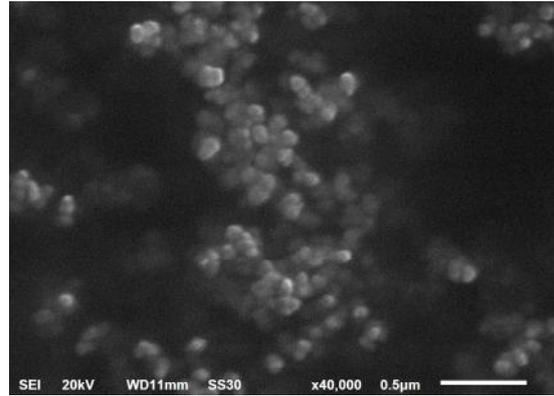
area between silica particles (Lee *et al*, 2005).

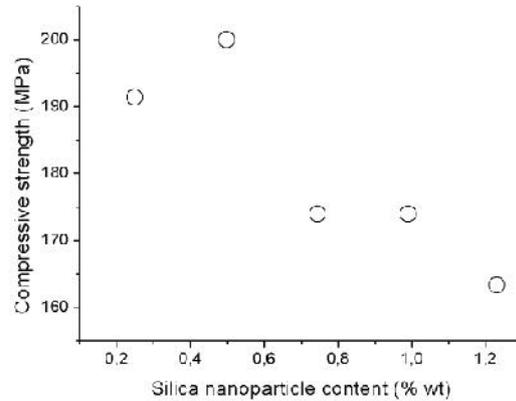**Figure 2.** SEM image of nanosilica with the average diameter is 74 nm

Figure 3. The compressive strength tends to improve as nanosilica loading (%wt). At nanosilica fraction of 0.497%wt, a maximum compressive strength of 200 MPa was obtained.

For all fraction of the nanosilica, the compressive strength of the composite increases owing the occurrence of contact between particle (silica) and polymer (Fig. 2). A maximum strength of 200 MPa was obtained for fraction of nanosilica of 0.496% g/g or increases about 23% compared to composite without nanosilica. This strength was better than that have been done, such as agriculture-nanosilica composite (57 MPa) [3] and solid waste-polyvinyl acetate (PVAc)-nanosilica composite (85 MPa) (Masturi et al, 2011(a)) and leaves waste-polyurethane (PU)-silica composite (70.5 MPa) (Masturi et al, 2011(b)). The strength was also better than that of some bricks and stones such as slate with sandstone (151.6 MPa), silty slate (132.7 MPa), limestone (80.2 MPa), dolomite (100 MPa) and some concretes with Portland cement having strength of 52.5 Mpa (Sastre et al, 2008; Moh'd, 2009; Chang et al, 2006; Alilou & Teshnehlab, 2010).
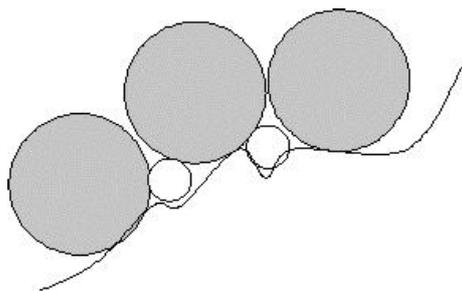
Figure 4. Illustration of polymer (*line*), solid waste (*gray-large circle*) and nanosilica (*white-small circle*) position in the composite. Because of the far smaller size, nanosilica can fill to the void of polymer and solid waste and ultimately enhance the contacts amount of the composite.

The occurrence of the enhancement strength can be understood in the term of the occurrence of interfacial area or contacts between silica and polymer, moreover the silica with far smaller size than solid waste particles may enter and fill to the void of PU-solid waste (Fig. 4). Even, at lower content, the nanosilica is dispersed by the water especially onto the carbonyl and amine groups of PU to form hydrogen bridges [12] governing the strength improvement of composite due to hydrogen interaction appearance between oxygen of silica and the active groups of PU (Hunt, 2008; Volkov et al, 1990), even they may form new covalent bonding due to temperature and pressure during hot-pressing process. The interaction also occurred between silica and some atoms of the polymer, such as C-N and C-O connected by the hydrogen bridges (Fig. 5). The appearance of all interactions above was further confirmed by FTIR Spectroscopy.
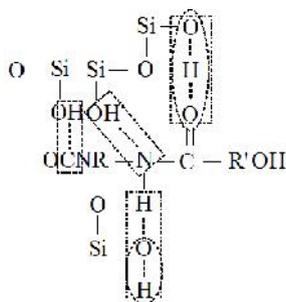

Figure 5. Van der Waals interaction between oxygen atoms of silica and some atoms in the active groups of PU (*dashed square*), and some hydrogen bridges occurred in the composite (*dashed ellips*). Both types of the interaction are very dominant in the enhancement of the composite compressive strength (Volkov et al, 1990).

The spectra were observed only from PU, nanosilica and PU-nanosilica composite (Fig. 6). Prior to PU and nanosilica mixed, in PU spectra, the peaks of 3328.9, 3126.4 and 2258.5 cm^{-1} and the peaks of 1508.2, 1595.0 and 1656.7 cm^{-1} originated respectively from amine group (N-H) from carbonyl (C=O) group (Fig. 6(a)). In addition, the appearance of peaks at 759.9, 812.0, 960.5 and 1109.1 cm^{-1} originated from C-C and C-N bondings. Meanwhile, in silica spectra the Si-O bonding was observed at the peaks of 806.3 and 1109.1 cm^{-1} (Fig. 6(b)). The occurrence of 3444.9 cm^{-1} is believed from O-H bonding of water attached in the silica owing hygroscopic condition.

As mixed with silica, some amine spectra of PU is shifted, i.e. from 3328.9 to 3402.2, from 3126.4 to 3130.3 and 2842.8 to 2848.7 cm^{-1} (Fig. 6(c)) As well, a peak of carbonyl, i.e. from 1595.0 to 1596.9 cm^{-1} and some peaks of C-C and C-N spectra, i.e. from 960.5 to 962.4 and 759.9 to 758.0 cm^{-1} are also shifted significantly and indicates that the effect of nanosilica addition in improving the composite strength is significant too. Microscopically, the occurrence of strength improvement is related to an energy perturbing active groups of PU and other bondings due to silica addition. This energy absolutely is a weak energy as shown from the small shift of the peaks and usually called as van der Waals potential (Hunt, 2008). This approach has been successfully done for the polyvinyl acetate-silica composite explanation (Masturi et al, 2011(a)).

Particularly, for the PU-silica composite the van der Waals interaction can be estimated from measuring the PU peaks shifting due to silica addition. Keeping this in mind and treating the relation (Tan et al, 2007): $E = \hbar c \kappa$ where $\hbar$ is Planck constant (~ 1.05 x 10^{-34} J.s.), c is speed of electromagnetic wave (~ 3 x 10^8 m/s) and κ is wave number of the bonding vibration (peak of the bonding), we find the van der Waals energy as: $\Delta E = \hbar c \Delta \kappa$ where $\Delta \kappa$ is the shifting of peak due to interaction appearance. From the argument, the van der Waals interaction between silica and amine and carbonyl groups respectively is 1.64 x 10^{-3} eV and 3.76 x 10^{-5} eV, while for C-C and C-N bondings the total van der Waals interaction is 7.51 x 10^{-5} eV.
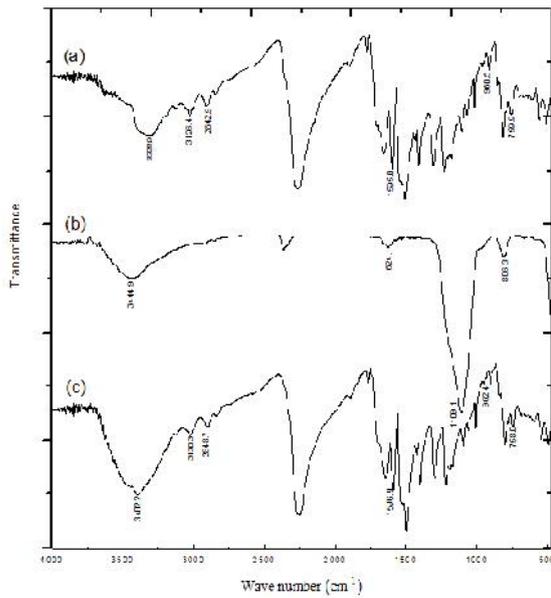
Figure 6. Spectra of (a) PU, (b) nanosilica and (c) PU-nanosilica composite. The small shifts observed at some spectra of PU due to silica addition indicates the occurrence of van der Waals interaction governing the strength enhancement.

Keeping the results above in mind, as far we can estimate the distance occurred between the atoms in the composite. Using Lennard-Jones relation (Krishnamurthy et al, 2006): $E_{vdW} = 4\varepsilon\left((\sigma/r)^{12} - (\sigma/r)^6\right)$. With data of several equilibrium bonding energies of several materials [21], i.e ε_{HH}=3.18x10^{-3}eV, ε_{CC}=2.86x10^{-3}eV, ε_{NN}=3.00x10^{-3}eV, σ_{OO}=3.36 Å, σ_{HH}=2.93 Å, σ_{CC}=3.47 Å and σ_{NN}=3.32 Å and using the Lorentz-Berthelot relation: σ_{ab} =($\sigma_{aa}\sigma_{bb}$)/2 and ε_{ab}=$\sqrt{\varepsilon_a \varepsilon_b}$ (Rouhaa & Nezbeda, 2009), furthermore the distances between oxygen of silica and hydrogen of amine group and between oxygen of carbonyl group and hydrogen bridge connecting silica and the oxygen (Fig. 4) can be estimated as respectively about 3.11 Å and 3.14 Å. As far, the distance of hydrogen bridges of silica to oxygen of C-O and nitrogen of C-N is respectively about 3.41 Å and 3.12 Å. Even though all the distances among the atoms were smaller than that of the equilibrium distances, it was believed there is no new bonding. This argument was confirmed by the absence of new peak occurring due to silica addition.

The compressive strength was also governed by temperature and pressure while fabrication. The involving of pressure physically makes the polymer to enter and fill to the pores of solid waste easily so the polymer distribution in the composite spreads more uniform and the distance among polymer, solid waste particles and silica particles becomes closer (Baldan, 2004). In this condition, the compressive strength-produced was larger as result of the more contacts between fillers (solid waste particles and nanosilica) and polymer and the greater van der Waals interaction (Lefevre &Joviet, 2009), meanwhile, the heat role can be understood in the term of the polymer viscosity decreasing as the increasing of temperature (Matyka et al, 2008). As the viscosity decreases, the polymer impregnation is more spread evenly so the amount of interaction area between particles and polymer is larger and as a result the compressive strength improves too.

As far, beside high compressive strength, this composite is also very lightweight material. With the density of 0.7 g/cm^3, it is very comparable to some woods usually used for building materials, such as Jati (*Tectona grandis*) and Mahoni (*Swietenia macrophylla*) woods having densities of 0.8 g/cm^3 and 0.7 g/cm^3 respectively (Soewarsono, 1990; Martawijaya, 1992). In conclusion, with the height of the compressive strength and the lightweight of the density, this composite is very adequate to be applied as building materials. Therefore, the utilization of the composite in a massive-scale promises solution not only for solid waste problem in several cities, but also for deforestation activity as result of high use of the woods.

CONCLUSION

A solid waste–polyurethane (PU) composite was synthesized by simple mixing and hot-press methods with nanosilica as reinforcement to improve the compressive strength. The solid waste is consisting of paper and dried leaves. The temperature and pressure of hot-press operated were 5 metric tons and 80°C respectively for 20 minutes. Prior to nanosilica addition, a maximum compressive strength of PU-solid waste composite is 160 MPa for solid waste volume fraction of 87.15% that called the optimum volume fraction. For further strength, into the optimum fraction of solid waste and PU, nanosilica with average diameter size of 74 nm was added and obtained a maximum compressive strength of 200 MPa for nanosilica fraction of 0.496% wt or increases about 23% of that without nanosilica. This strength was better than that of composite have been produced,

such as agriculture waste-silica composite (57 MPa), solid waste-PVAc-nanosilica composite (85 MPa) and some stones such as slate with sandstone (151.6 MPa), silty slate (132.7 MPa), limestone (80.2 MPa), dolomite (100 MPa) and some concretes with Portland cement (52.5 MPa). The strength enhancement due to nanosilica addition was corresponding to the van der Waals interaction occurred between nanosilica and PU where its magnitude was briefly shown by Lennard-Jones potential relation and the peaks shifting of the FTIR spectra. The composite was also measured its density and obtained the density is about 0.7 g/cm^3, that is very lightweight and comparable to Jati (*Tectona grandis*) and Mahoni (*Swietenia macrophylla*) where their densities are 0.8 g/cm^3 and Mahoni 0.7 g/cm^3 respectively. Thus, the composite is very adequate and potential for building material application to compete the woods since it has adequate strength and lightweight.

ACKNOWLEDGEMENT

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