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Research paper

Thermal Degradation Study of Waste Polymer Matrix Polypropylene and Polyvinyl Chloride as Polymer Matrix Filled Rice Husk Decking Structure

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Abstract

The aim of this study is to find another alternative material to replace the additives of polymeric materials. From previous works, woodchips are used to act as filler instead of rice husk. Thus, in this case, the woodchips is being exchange with rice husk and mixed with the waste polymer in order to reduce the cost. This study is about the effect of thermal towards the mechanical and physical properties of this WPC. Therefore, heat test and UV Irradiation Exposure test were conducted on this wood polymer composite (WPC). Then, three parameters were being examined which were difference in density, hardness and physical properties after undergoing heat test and UV Irradiation Exposure test. The density and hardness appearances from both test only had slightly reduction and it can be considered as negligible. The physical changes were not too apparent such as crack that would lead to failure even after being heated and exposed to the UV light for a long period. Thus, it proves that rice husk could replace woodchips in order to be used as decking structure.

Keywords: *Heat test; polypropylene; polyvinyl chloride; thermal degradation; UV irradiation exposure*.

1. Introduction

The changes in physical appearance and mechanical properties of the polymers due to the thermal degradation such as heat and weathering (commonly ultra violet) are being investigated. The materials involved in this investigation are polypropylene and polyvinyl chloride. Polymer is mixed with the filler from waste material such as rice husk. It is known as Wood Polymer Composite (WPC) and fabricated as decking.

Deck is a flat surface which can sustain load, it has the same function as floor, but it usually constructed for outdoor applications. The construction is higher than the ground, and usually connected to the building. Decking structure is originally designed for ships at first, but nowadays it is applied for building too. Normally, the deck structure will deteriorate physically and mechanically upon ultra-violet or heat exposure. Decking, porch flooring and siding are manufactured from rice husks—an agricultural waste product—along with salt, mineral oil and plastic polymers [1].

According to [2], between the various component of waste in landfills, about 20% to 30% of the polymeric materials composites were disposed. However, polymeric material had high resistance toward the microbial degrading, it will remain in the landfill as semi-permanent waste. So, it will take longer time to be degraded since the polymer material are not easily to be degraded.

Waste polymer is generally defined as unwanted or unused polymer after a primary use. Polymer is known as non-biodegradable since it cannot be degrade easily. Usually, it will take a long time to degrade due to high resistance towards chemical and bacteria. A polymer is a long chain molecule made up of a repeated pattern of monomers. Polymer can be divided into three groups which are elastomer, thermoplastic and thermosets. Elastomer can be described as a material that can return to its original state after undergoing stretching at least twice of its original length under room temperature. Thermoplastic is plastic that can be re-heated and re-formed into another shapes without going through any significant changes towards its properties. Meanwhile, thermoset can be known as plastic that cannot be re-heated or re-formed into another. In addition, virgin or origin petroleum based on polymer has many types such as Polypropylene (PP), Polyvinyl Chloride (PVC), Low-density Polyethylene (LDPE), High-density Polyethylene (HDPA), Polyethylene (PE) and Polystyrene (PS).

Polypropylene (PP) is one of the existing polymers that are widely used nowadays. Thermoplastic PP is also involved in the production of decking structure. Usually, for the decking structure, rice husk is used as filler to the matrix polymer of polypropylene. Rice husk is used to replace the woodchips in order to save cost. Polypropylene is very susceptible to thermal degradation, even at normal temperatures and must always be protected against thermal degradation. Thermal degradation causes chain scission and the reduced chain length reduces the molecular weight. This can considerably change the mechanical properties leading to highly reduced ductility and embrittlement and possible service failure [3].

Other than PP, Polyvinyl Chloride (PVC) is one of the most important polymers that are being used as building structure such as decking structure. PVC is very susceptible to thermal degradation, particularly during processing and can suffer from extensive property loss if not adequately protected against thermal degradation during processing [3]. PVC or usually known as ‘vinyl’ in certain country such as in Europe-are widely used nowadays and it hit the world’s third-most produced synthetic polymers, after PE and PP. PVC is divided into two basic forms which are rigid and flexible.

PVC with rigid form is usually used in construction of pipe and in profile applications such as doors. PVC with flexible form is usually used in plumbing. PVC can also be mixed with the rice husk in order to form the decking structure as well as PP.

Paddy rice is cultivated in every continent except Antarctica due to the inappropriate climate for paddy cultivation. The production of rice was dominated by Asia since it was staple food for Asian. Besides that, rice is the only food crop that can be grown during the raining season which are commonly experienced by Asia. Paddy, on an average, consists of about 72% of rice, 5-8% of bran and 20-22% of husk [4]. Each ton of paddy rice can produce approximately 200 kg of rice husk, which on combustion produces about 40 kg of ash [5].

Rice husk has been widely used nowadays, especially as building material and fertilizer. Apart from that, it is also used to replace woodchips in the particleboard, along with decking structure. In 2015, Husk-To-Home Team did some innovation towards these particleboard which were previously made from woodchips. Then, it changes to rice husk in order to prevent the termites from eating the wood [6]. On the other hand, it made from hard materials such as silica and lignin. The main constituent in the RH has 70-90 % organic matter such as cellulose, lignin etc. and remaining minerals like silica, alkalis are also present in it [7]. The silica make termites face difficulties to consume. In addition, rice husk is cheaper than woodchips. Thus, the main function of rice husk is act as filler for composites material in various polymer matrixes besides increasing the density of the material

The composite material used in their decking floor product are consist of wood and plastic mix. Roughly, their percentage of material are 50% wood, 40% recycled plastics and 10% glue [8]. The recycled plastic is actually refer to the waste polymer. All of the material mentioned will be mixed together and then extruded to form either a hollow or solid decking board.

2. Material and Methods

2.1. Material

The composites were made of from combination of waste polymer and rice husk (RH). The waste polymer used was Polypropylene (PP) and Polyvinyl Chloride (PVC). The RH is pulverized into flour with 80 mesh sieve under 110 micron. Then, the RH flour is dried in hot mixer at 80°C for 30 minutes to remove the moisture. Then, PVC or PP (either one), RH flour and a little additives (plasticizer, PE wax, Ca/Zn stabilizer, TiO_2 as UV stabilizer) is weighed to ensure the composition is accurate to 30% of RH and 70% of waste polymer. After that, the mixture is mixed in hot mixer and discharged to cooling mixer. Then, the mixture is compounded to produce WPC pellets. Finally, the last process is injection moulding to produce specimen. The length was about 122.5 cm, 2.5cm of thickness and 14.7cm of width.

2.2. Heat Test

In this test, its aim is to measure the thermal stability. Oven test would be conducted by using Universal Oven (Memmert UN 160 Universal Oven 161L UF160). Two sizes of samples are prepared are 1cm X 1cm X 1cm (±0.2cm) for Density Test and 2cm X 2cm X 1cm (±0.2cm) for Shore D Hardness Test and Physical Observation Test. Heat test would be carried out at various temperature which are 50°C, 60°C and 70°C respectively. The temperature is advised to be in this range since polymer has low glass transition temperature, T_g. In addition, the glass transition temperature for Polypropylene and Polyvinyl Chloride are 100°C and 81°C respectively. The characterization of this polymer for oven test are 5 hours, 10 hours, 15 hours and 20 hours.

After the Heat Test, all the samples were subjected to three different tests which are Physical Changes Test, Shore D Hardness Test and Density Test. The induced degradation was examined in terms of physical changes throughout different temperature by means of temperature.

2.2. UV Irradiation Exposure Test

In order to measure the stability of the application for recycled PP and PVC (as comparison), the simulation of sunlight irradiation exposure was conducted by using UV Weatherometer.

The UV irradiation exposure time set at 5000 hours, 10000 hours, 15000 hours and 20,000 hours with harsh equatorial condition with higher than ambient temperature of 27°C. This will eventually give more data and information on the effect of the UV irradiation exposure towards the stability of both polymer (PP and PVC).

Two sizes of sample were prepared for this method. Firstly, 1cm X 1cm X 1cm (±0.2cm) for Density Test. Sample size of 2cm X 2cm X 1cm (±0.2cm) were prepared for Shore D Hardness Test which required bigger size in order to calculate average values of hardness number.

2.3. Shore D Hardness Test

For plastic, one of the examination test that can be conducted is Shore D hardness measurement [9]. The instrument for hardness test is Durometer (HBD 100-0). The hardness of irradiated sample; before and after each treatment were measured by using Shore D Durometer. It would determine the hardness of sample of both test; UV irradiation and Heat Test. Thus, the comparison can be made. At least five point from the surface of the sample must be measured by Shore D Durometer. Thus, the average of the hardness of the sample can be obtained and calculated. Usually, for Shore D Hardness, the standard is ASTM D2240 or ISO868 [10].

2.4. Density Test

The density test would be conducted by using water as immersion liquid. The sample for this test is 1cm x 1cm x 1cm. The density would be measured by using AND Weighing HR100A Analytical Balance after being exposed to UV irradiation and Oven Test. The method for the density test, which is by immersed it with water is used [11].

2.5. Physical Changes

The changes in physical properties can be observed by using OM under 50x magnification. OM is used to observe the existence of char, colour changes and pin hole, crack or any changes that occur on the surface of sample. Once in the environment, plastic waste is subjected to solar radiation, UV rays and heat, which affect their surface as well as to some extent their bulk properties [2].

3. Results and Discussion

3.1. Density Analysis

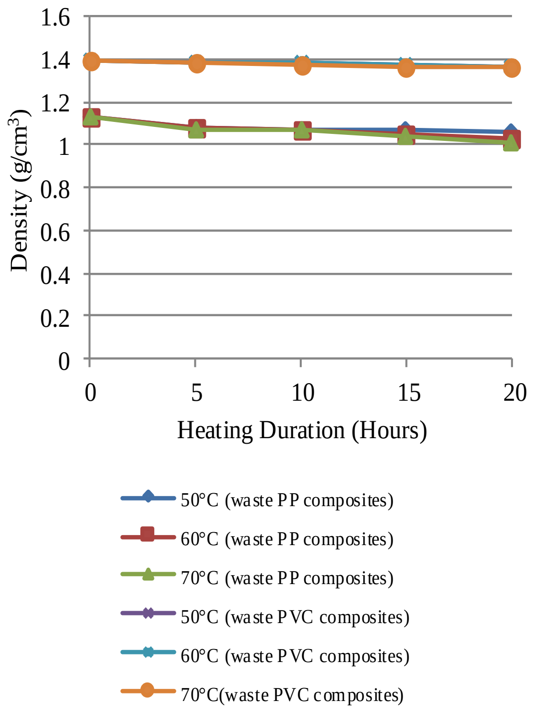


Fig. 1: Density against heating duration for both waste PP and waste PVC composites for heat test

Based on the Fig. 1, it show the graph of density against heating duration for both waste PP and waste PVC composites, the three line above were indicated the density of waste PP composites and the three line bottom were represented the density of waste PVC composites.

By comparing both waste PP and waste PVC composites, the density reduction experienced by waste PVC composites was lower than waste PP composites. This was due to PVC itself was intrinsically heat unstable and it could even decompose during processing. However, PP was very tolerant with heat; even under extreme conditions it will only decompose to lower molecular weight paraffin which are elementally compatible with the base material [12].

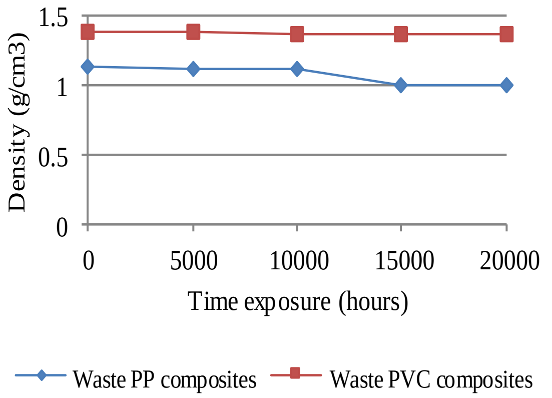


Fig. 2: Density against time exposure for both waste PP and waste PVC composites for UV test

Bulk density decrease with increase rice husk addition because the large the RH organic matter content, the greater the porosity and shorter the past among particles for gas diffusion [13]. Therefore, RH was actually fill out the vacancies among the particles of polymer matrix. By comparing both samples, waste PP composites have low density compared to the waste PVC. It was due to the density of polymer itself, the density of true PP was lower than true PVC.

3.2. Shore D Hardness Analysis

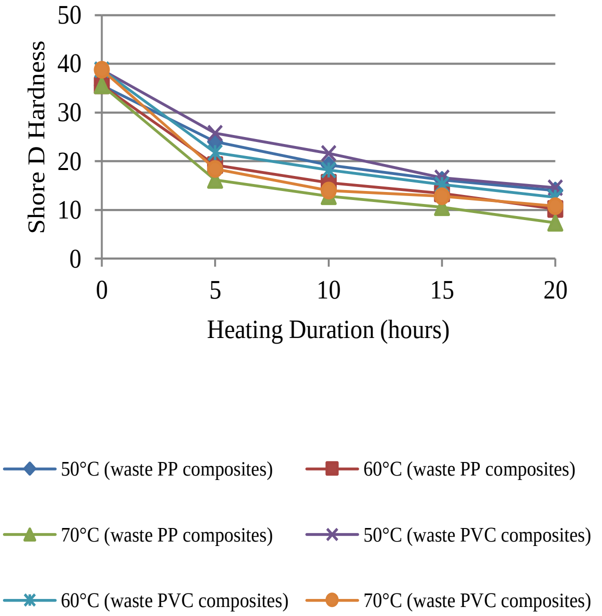


Fig. 3: Shore D hardness against heating duration for heat test of waste PP and waste PVC composites

A hypothesis could be made which is as the heating duration increased, the shore D hardness become lower. It was due to the structure of the sample itself after being heated and also the strength of the polymer which contributes to the decreased in the value of hardness. During tempering or heat treatment, the hardness would decrease [14]. Decreasing of hardness value is due to the poor adhesion at the surface between particles and polymeric matrix [15].

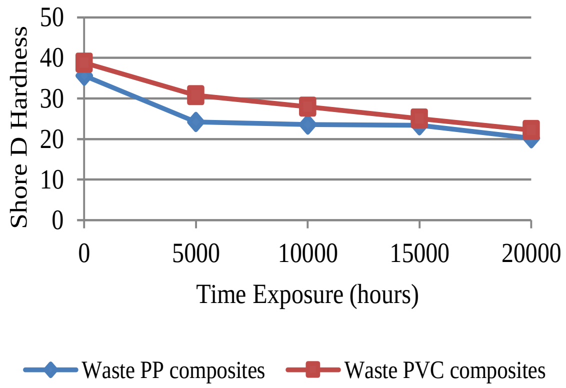
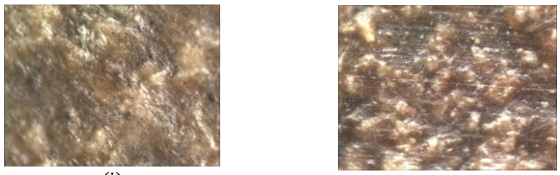


Fig. 4: Shore D hardness against time exposure for UV test of waste PP and waste PVC composites

The relationship between hardness and time exposure were inversely proportional. It was hypothesized that polymeric chains and branches were destroyed by UV radiation, affecting the mechanical performance of the polymer [16]. One of the mechanical performance was hardness. Therefore, due to the destruction of the polymeric chain, the hardness decreased as the sample was exposed to the UV light [17].

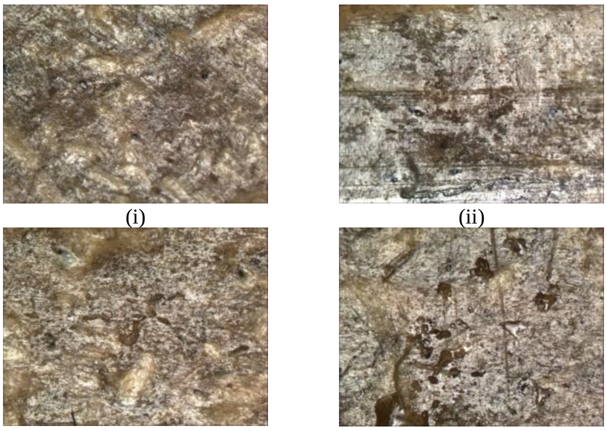
3.3. Physical Changes



(i) (ii)

Fig. 5: Morphology surface of initial waste PP composites under 50x magnification of OM

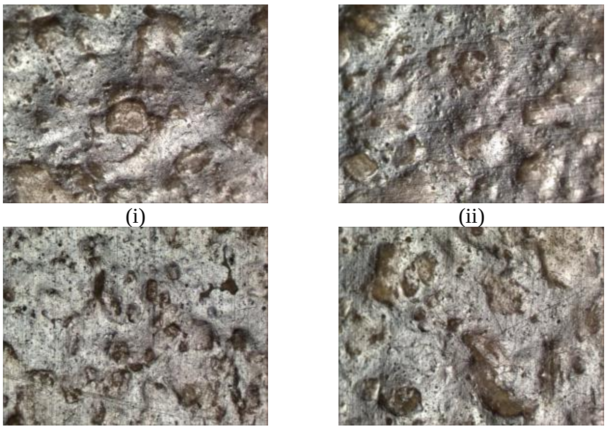
Evidently, Fig. 5 (i) shows the upper surface is dull in colour, no crack or void. The distribution of RH underneath the polymer could also be observed. The cavities does not exist at the beginning. However, if compared to the waste PVC composites, the surface of the waste PP composites seem rough and groovy when touched. The sample of waste PP composites were a little bit hard at first. The colour of the initial waste PP sample were light brown, although under the OM observation was more to the darker shade.
By referring to Fig. 5 (ii), the surface of the waste PP composites seem rough under OM. However, when observed by naked eyes, the surface was too smooth. The surface does not feel uneven at all when touched. The colour of the waste PVC sample was same as observed under the OM, which was dark brown.
The overall results for physical changes experienced by both waste PP and waste PVC composites after being heated were colour changes, existence of pore and existence of cavities. The cavities were developed from the combination of pores and pin holes.
For the colour changes for waste PP composites, the colour was light brown at origin. After being heated for a while, the colour would turn to yellow brown colour. Finally, the colour become yellowish. The sample experienced the colour changes, where the colour become faded as the heating being continued.
By comparing both colour changes, both waste PP and waste PVC showed that the colour being degraded after being heated. However, the colour changes not happened drastically. It was degrade slowly. The colour changes occur due to the oxidation that happened during heating process, where the polymer chain of both PP and PVC react with oxygen [18]. These oxidation would lead to degrade and the results was decolourization.



(i) (ii) (iii) (iv)

Fig. 6: Morphological surface of waste PP composites under 50x magnification of optical microscope after being exposed to the UV light for (i) 5,000 hours (ii) 10,000 hours (iii) 15,000 hours and (iv) 20,000 hours

Referring to Fig. 6, it showed the difference that being detected by using OM when the sample of waste PP composites being exposed to the UV light. Every increment of 5,000 hours were being recorded.
When the sample of waste PP composites were exposed to the UV light for about 5,000 hours, the sample were shown in the Fig. 6(i). There were exist some cavities. The cavities were looked like dotted. The colour changes to a little bit brown. The surface also seem rough than the initial surface.
After being exposed to the UV light for about 10,000 hours, the sample were shown in the Fig. 6(ii). The existence of cavities were become more clear and the increased in number. The combination of the cavities, become lines. The initial colour were decolourised, paler than the previous.
Fig. 6(iii) shown the sample of waste PP composites after 15,000 hours of exposure towards the UV light. The cavities become larger than the previous one and the colour was become dark grey. The RH appeared to the surface. The combination of lines would develops crack.
After 20,000 hours of exposure to the UV light irradiation were shown in Fig. 6(iv). The colour of waste PP composites become dark grey. The lines were more apparent than the previous one. The cavities were keep increase in size once being exposed to the UV light.
Photo degradation was a term that refer to colour fading [16]. Actually, the colour exist due to the chemical bonds. The UV rays can break down the chemical bonds and contributed to fade the colours. Waste PP composites experienced photo degradation, therefore the changes in colour happened.
Existence of pores and cavities was due to the shrinkage that experienced by RH after being heated [19]. Before the heating, the mixture of RH and waste polymer were compact. However, after being heated, the size of RH become degraded a little by little. The increased number of cavities caused the pores to exist.



(i) (ii) (iii) (iv)

Fig. 7: Morphology surface of waste PVC Composites under 50x magnification of optical microscope after being exposed to the UV light for (i) 5,000 hours (ii) 10,000 hours (iii) 15,000 hours and (iv) 20,000 hours

According to the Fig. 7, the four pictures showed the changes that were detected for waste PVC composites after the samples were being exposed to the UV light. Every changes in increment of 5,000 hours were captured. Fig. 7 (i) showed some appearance of RH on the surface. The colour of waste PVC composites sample were decolourised and became shining grey. Next, referring to Fig. 7 (ii), the colour of sample were same as the previous one which were shining grey. However, the cavities appeared were more than the previous one and it could be seen more clearly. That was happened when the sample were being exposed to the UV light for 10,000 hours.
In Fig. 7 (iii), it shows the sample after being exposed to UV light for about 15,000 hours. The pores started to appear too instead of cavities. The colour become dull grey. Last but not least, Fig. 7 (iv) shows the condition of sample of waste PVC after being exposed to UV light for about 20,000 hours. The sample started to crack on the surface. The crack exist because solar UV radiation is well known to decrease the impact strength of the polymer. As the surface layers of the plastic material degrades, the titanium dioxide powder used as an opacifier was gradually released and may even form a surface layer loose enough to be rubbed off. This will lead to "chalking" or known as cracking of extensively exposed PVC siding materials. Both the tensile strength and the extensibility of rigid PVC samples also decreased with the duration of exposure to solar UV radiation and the material finally embrittles [20]. The colour was remain dull grey.
The reason of decolourisation was because UV rays breaks the chemical bond that exist in the waste PVC composites. Therefore, the colour become pale after being exposed to the UV light. The polymer absorbed energy from light, thus crystalline the polymer matrix. This could cause the surface become shiny. The shrinkage of the RH after being exposed to the UV contribute to the existence of the pores and cavities. UV light conduct heat and thermal towards the sample and lead to the shrinkage of RH. The shrinkage make space between the mixtures which lead to the existence cavities.

4. Conclusion

In conclusion, the objective of this experiment had been achieved after conducted both Heat Test and UV Irradiation Exposure Test. Firstly, the thermal stability of the both waste PP and waste PVC filled rice husk filler known as WPC that were used for industrial building structure had been measured by using both test. Secondly, the changes in physical and mechanical properties of WPC upon heat and UV irradiation exposure had been determined. These both objective were achieve once the result for density, hardness and physical changes were obtained.

In order to examine the thermal degradation effect towards waste PP and waste PVC composites, two experiment conducted which were Heat test and UV Irradiation Exposure. About three parameter is measured which were density, shore D hardness and physical changes.

For heat test, three temperature was set up which were 50^{o}C, 60^{o}C and 70^{o}C. The sample being heated for 20 hours, the parameter was examined every 5 hours. About the density, there only a few reduction occur although after 20 hours heating. Waste PP composites only decreased about 10% from the initial and 2.1% for waste PVC composites. On the other hand, the shore D hardness result show the decreased in value for both composites, and the reduction was over 50%. Between these two composites, waste PP were low in hardness compared to the other one. After being heated, a few things were difference from the initial one such as the colour changes, pore and cavities exist and the RH appeared to the surface of sample.

For UV exposure, the sample were being exposed to the UV light by using UV Weatherometer for about 20,000 hours. Every 5,000 hours, the sample were being take out to be examined for three test. For density, the result was nearly same to the density of heat test. Both were decreased. In hardness, the reduction for both type of samples were below than 50%. For physical changes after being exposed to the UV light, the RH were appeared to the surface. The cavities were exist, and it increased in number. Then, it would lead to for line. The line would develop cracks.

Acknowledgement

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