Studies on degradation of rice husk ash filled in polypropylene composite films under natural weathering condition

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Abstract. Natural weathering of rice husk ash filled in polypropylene composite films has been investigated by exposing the samples to a tropical clime for 4 months with max-min temperature 22 - 30°C and relative humidity 75%. In this study, the film composites filled with rice husk ash for decay to get the composites that has good mechanical performance after exposure in natural weathering. Rise husk ash filled in film composite polypropylene effect of filler loading was 1, 2, 3, 4 and 5% and compare with neat composite. The silica from rice husk ash was isolated with acetic acid. The weathered film composites polypropylene was investigated before and after exposure and analysed the morphology with FTIR and SEM. Mechanical test for the film composites polypropylene take place for tensile strength and percentages of elongation at break. The result show that the tensile strength and percentages of elongation at break decrease after natural weathering. The average tensile strength of film composites polypropylene decrease about 64.54 ± 17.50% and the elongation at break of film composites polypropylene decrease about 49.33 ± 15.28%. The morphology of film composites change structure of chemical and fracture surface after natural weathering.

1. Introduction

Now day, the used natural fibers as reinforcement/filler in composites, such as agriculture solid waste has become a concern for researchers, academics and also industry. These types of agricultural solid wastes have been widely used as reinforcement in thermoplastic polymers and thermoset polymers [1]. The advantage of using natural materials as fillers because of cheap, renewable, and easily biodegradable, and when these fillers are added to polymer composites, they will provide better mechanical composite properties compared to synthetic fibers [2]. Today, the use of natural fibers in strengthening composite polymers is very popular in automobiles, cosmetics and applications for packaging [3].

In material products that use natural fibers, degradation to the environment can occur due to the influence of UV include sun light, moisture, ozone and oxygen molecules. Damage to these material products can damage the chemical structure in the material. This occurred because in biocomposite
materials containing unsaturated chemical bonds, these bonds can easily be attacked by ozone and oxygen molecules [4]. Ozone attacks can cause colour loss and cracks on the surface of composite materials. While the oxygen attack on the surface of the composite can cause hardness, crack and brittle, so the composite polymer will lose cross linking and will be damaged [5].

Silica is a filler material added to the polymer as a matrix which has excellent mechanical properties, especially having high crystalline. Silica obtained from rice husk ash has a higher content than rice straw and rice husk [6]. The addition of various concentration of silica as reinforcement in polymer composites also greatly affects the resistance to the environment, especially as silica is still in the form of aggregates in polymer composites [1,7]. This research has studied the environmental resistance of composite polypropylene filled with silica from rice husk ash effect of natural weathering. In this study, silica has isolated from rice husk ash with acetic acid. As changes to environmental influences such as rain, heat and air humidity on polypropylene composite films has been studied natural weathering and changes to mechanical properties and morphology.

2. Experiment

2.1. Materials description
The filler used in this study was silica that has isolated from rice husk ash with acetic acid 3 M with rotated 500 rpm. Polypropylene was provided, as matrix that has density 0.9 g/cm$^3$, and melt flow index 3.5 g/10 minute. The filler loading in the polypropylene composite films were 1, 2, 3, 4 and 5% of silica isolated and as a comparison polypropylene was used without fillers.

2.2. Method
Polypropylene composite films which have been cut to size for mechanical properties was hung on a shelf, then the rack was placed on the roof, so that a direct sample of environmental influences such as rain, sunlight and wind (Figure 1). The sample was taken after four months of exposure to sunlight. The samples were taken to analyse the tensile strength and flexural strength as mechanical properties, and morphological analyses performed were performed with FT-IR and SEM.

![Figure 1. Polypropylene composite films exposure on the rack for natural weathering.](image)

2.3. FTIR analysis
The FTIR spectra were used to identify the functional group of polypropylene composite films. The analysed were recorded on Fourier Transform Infrared Spectrometer Shimadzu Prestige 6400. The polypropylene composite film was put on the sample holder to get records the functional group. Polypropylene composite film was measured in the wavelength range from 4000 cm$^{-1}$ to 400 cm$^{-1}$ [8].

2.4. SEM analysis
The tensile fracture surface morphology of polypropylene composite films before and after natural
weathering was determined by scanning electron microscopy (SEM). The polypropylene composite films were kept in an oven for overnight at 60°C for removal moisture content. Observation of the polypropylene composite films was dipped with gold.

2.5. Mechanical properties
Mechanical properties for polypropylene composite films before and after natural weathering include tensile strength and elongation at break. The mechanical test conducted using Instron Universal Testing Machine, according to ASTM D638. The samples composites film tests carry out at 10 mm/min at 25°C. Tensile strength and elongation at break were recorded from the software.

3. Result and discussion
3.1. Functional group of polypropylene composite films
Fourier transform infrared (FTIR) spectroscopy was used to determine the development of degradation polypropylene composite films, such as carbonyl groups and vinyl groups, and to determine the changes in PP crystallinity of composite films. Functional groups of polypropylene composite films before and after natural weathering for four months are presented in Figure 2. The spectra of polypropylene composite films before and after weathering show not change significantly after exposure in UV condition in natural weathering. The peak at 2900 cm⁻¹ indicated that present of functional group of –CH₂-, it is show the vibration type of C-H stretching [9]. At this peak showed clear that not change the wavenumber for all composite films before and after natural weathering. C-H stretching of alkane vibrations of methylene groups also investigated in this peak (2900 cm⁻¹). In this peak was chosen as a reference peak because it changed the least during aging. In the double bond area, peak at 1723 cm⁻¹ at both spectra were assigned to stretching C=O from acetyl and uronic ester.

The peaks were sharp at 1643 cm⁻¹ for silica from rice husk ash reflected for amide. The amide band represented 80% of the C = O stretching amide group, combined into N-H bending and C-N stretching mode. Vibration depends on the nature of the hydrogen bonds involved in groups C=O and N-H and the secondary structure of the protein. In the fingerprint area, there are many sharp peaks observed from both spectra. Bands in the range of 1450-1370 cm⁻¹ show the symmetrical C-H and asymmetrical deformation. The 1200-1000 cm⁻¹ region represents C-O stretching and deformation in cellulose and lignin.

Ismail et al, investigated that the functional groups from the biomass such as silica from rice hush ash would act as chromophores (degradation initiators) and the photo oxidation when exposure in UV [10]. This proves that the linkages formed between silica and polypropylene matrix was destroyed during weathering [11].

The increase of carbonyl groups concentration after exposure time the carbonyl index was roughly lower for the polypropylene composite films. Formation of vinyl group is an indication of polypropylene chain scission. From the Fig. 2 shows the increase in vinyl group concentration based on the peak at 900 cm⁻¹.
3.2. Fracture surface of polypropylene composite films

Figure 3 show the fracture surface of the polypropylene composite films before and after natural weathering for four months. The fracture surface not change in neat polypropylene before and after weathering because no filler in the matrix. It is show in the Figure 3 a and b. On the other hand, for the polypropylene filled with silica from rice hush ash show the silica (white colour) start regardless of the matrix (red circle). The presence of silica that appears after four months exposure indicates the effect of weather on the composite films during natural weathering. This led to poor interaction between silica and polypropylene as matrixes.

High loading silica in polypropylene matrixes was shown the effect of compatibility between filler and matrix poor. It can be observed that all the polypropylene composite films were highly degraded. All of the surface composite films were rough with formation of surface crack, which have an appearance similar to a mosaic pattern. The high silica content in the polypropylene the roughness of the surface polypropylene composite films also increase with formation of more micro crack. Increase weathering time for the polypropylene composite film will be effect of the crack because of activated of sun light to give off oxidizing moieties [11].

Figure 2. Functional group of polypropylene composite films (a) before and (b) after natural weathering.
Figure 3. SEM image for polypropylene composite film before and after natural weathering.
3.3. Mechanical properties of polypropylene composites films

Mechanical test of polypropylene composite films before and after weathering include tensile strength and percentage of elongation at break. Figure 4 show the change in tensile strength of polypropylene composite films after natural weathering. The high silica content in the polypropylene composite films the higher the tensile strength before weathering. The increase in tensile strength of the polypropylene composite films before weathering is due to the filler shape of silica from rice husk ash which can improve the ability of polypropylene to support stress transfer from polymer matrix. The shape and structure of filler actually give better interaction between filler and matrix and thus provide a higher degree of reinforcement [10]. Ismail et al, 2008 also employed that the silica contains has a large number of silanol groups on the surface that gives strong interaction between filler and polymer matrix. And give rise to a high tendency for filler agglomeration in the polymer matrix.

But after natural weathering, the tensile strength of polypropylene composite films decreases significantly. The large drop of tensile strength led to physical deterioration of polypropylene and caused the lowest tensile strength after weathering for 4 months. During weathering, UV oxidation would be break the chain of polymer matrix by photo oxidation process [11]. The chain scissions occurred after degradation of polypropylene composite films attack by oxidation under UV exposure. Scissions of the larger molecular chains increase the number of shorter polymer chains, a situation that would lead to fewer entanglements and cause the decrease in tensile strength [10,12].

The decrease of tensile strength after weathering was attributed incompatibility between silica filler and polypropylene matrix. In this case, shown that the weaker between polypropylene and silica filler interaction. The average tensile strength decrease of polypropylene composite films is about 64.54 ± 17.50%.

![Figure 4. Tensile strength of polypropylene composite films before and after natural weathering.](image)

The change of elongation at break before and after weathering of polypropylene composite films has shown in Figure 5. From the figure, for the polypropylene composite films before weathering, the elongation at break decrease when increasing the silica content. On the other hand, after weathering all the composite films drop in elongation at breaks. The average drop of elongation at break on the polypropylene composite films is about 49.33 ± 15.28 %. It show that very clear elongation at break
decrease after weathering is caused by chain scission in the composite films. It is caused by the breakdown of tie chain molecules and entanglements and especially detrimental to the ductility of the polymer matrix [10,11].

![Figure 5](image-url)  
*Figure 5.* Elongation at break polypropylene composite films before and after natural weathering.

### 4. Conclusion

Polypropylene composite films were prepared by silica from rice husk ash that isolated with acetic acid. The polypropylene composite films have studied the effect of natural weathering on morphology and mechanical properties. The results showed that the silica from rice husk ash play a role in improving the stability of polypropylene composite films slightly, but the relationship between shape, size, the treatment of the silica from rice husk surface and preparation method of composites and stability of polymer needs further research. FTIR analyses have showed that after weathering the polypropylene composite films change in the chemical functional group. From SEM analyses on the surface, the photo oxidation of materials begins from the surface and then develops along the depth gradually. The mechanical properties of composites decrease after exposure for 4 months. The tensile strength and elongation of composites after natural weathering high decrease because the filler and matrix polypropylene was not compatibility.

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