

## EFFECT OF WEATHERING ON FUNCTIONAL GROUP AND MECHANICAL PROPERTIES OF POLYPROPYLENE-KENAF COMPOSITES

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### ABSTRACT

**EFFECT OF WEATHERING ON FUNCTIONAL GROUP AND MECHANICAL PROPERTIES OF POLYPROPYLENE-KENAF COMPOSITES.** The functional group and the mechanical properties of unweathered and weathered polypropylene (PP)-kenaf composites have been analyzed by Fourier-Transformed Infrared Spectroscopy (FT-IR) and Universal Testing Machine. The composites have been prepared from PP(60 %w) + kenaf (40 %w) and PP(60 %w) + kenaf (40 %w) + maleic anhydride grafted polypropylene(MAPP) (1 %w) by blending method using laboplastomill mixer at 175 °C for 8 minutes then the blend was pressed by using hotpress at 175 °C, for 8 minutes with pressure of 50 kgf. Weathering sampling periods is 5.5 months. Surface chemical analysis of PP-kenaf and PP-kenaf-MAPP composites using FT-IR showed that lignin content decreased and surface oxidation (carbonyl content) increased during exposure. PP-kenaf and PP-kenaf-MAPP composites weathering result in reduced strength properties

**Key words :** Weathering, Polypropylene-kenaf composites, Maleic anhydride polypropylene

### ABSTRAK

**PENGARUH PENJEMURAN TERHADAP GUGUS FUNGSI DAN SIFAT MEKANIK KOMPOSIT POLIPROPILEN-KENAF.** Gugus fungsi dari polipropilen (PP), kenaf, komposit PP-kenaf tanpa dan dengan penjemuran telah dianalisis menggunakan *Fourier-Transformed Infrared Spectroscopy (FT-IR)* dan sifat mekanik diuji menggunakan *Universal Testing Machine (UTM)*. Komposit dibuat dari PP(60%w) + kenaf (40%w) dan PP(60%w) + kenaf (40%w) + *Maleic anhydride polypropylene (MAPP)* (1%w) ; dengan cara mencampur menggunakan alat *laboplastomill mixer* pada suhu 175 °C selama 8 menit, kemudian hasil pencampuran di pres menggunakan alat *Hotpress* pada suhu 175 °C, selama 8 menit juga dengan tekanan 50 kgf. Penjemuran cuplikan dilakukan selama 5.5 bulan. Analisis kimia permukaan pada komposit PP-Kenaf dan PP-kenaf-MAPP menggunakan *FT-IR* memperlihatkan kadar lignin menurun dan kadar karbonil meningkat selama pemaparan. Penjemuran komposit PP-Kenaf dan PP-kenaf-MAPP menurunkan kekuatan komposit.

**Kata kunci :** Penjemuran, Komposit polipropilen-kenaf, *Maleic anhydride polypropylene*

### INTRODUCTION

Kenaf (*Hibiscus cannabinus L.*) is an annual plant, has been found to be an important source of fiber composites and other industrial applications. They have applications in textiles, geotextiles, fiberboard, and pulp. The kenaf based fiber has high potential as a reinforcing fiber in thermoplastic composites because of its superior toughness and high aspect ratio in comparison with other fibers. A single fiber of kenaf can have a tensile strength and a modulus as high as 11.9 and 60.0 GPa respectively. These properties can vary depending on the source, age and separating techniques of the fiber.

The kenaf bast fiber is a composite made up of crystalline, thermoset polymer matrix (lignin and

hemicelluloses). Chemical composition are cellulose 44-57%, lignin 15-19%, pentosan 22-23%, ash 6-8%. Hemicelluloses from kenaf contains a backbone polymer of D-xylopyranose with side chains of D-galactose and L-arabinose. Lignin from kenaf contains a very high level of syringyl functionality. The function of lignin in plants is as encrusting agent in the cellulose/hemicellulose matrix. It is often referred to as the plant cell wall adhesive.

Chemical modification of the fiber to make it more hydrophobic, which improves its compatibility with non polar thermoplastic has been studied by Rowell *et al.* The results that maleic anhydride grafted polypropylene (MAPP) has been shown to function efficiently as a

coupling agent for kenaf-PP systems. The combination of covalent linkages and/or acid-base interaction between the MAPP and the -OH groups on the fiber surface results in good fiber surface-interface properties. Kenaf fibers are soft and non-abrasive and high filling levels are possible; 60 % (w/w) of fiber has been successfully incorporated in PP based composites.

Biocomposites need to resist weathering when used in outdoor applications. Agents for natural weathering include moisture, temperature, radiation (UV) and other forms of chemical interaction. Prolonged exposure of composites under these conditions will result in degradation of material properties. A variety of mechanisms contributes to the degradation process, e.g. mismatch in the coefficients of thermal expansion between the fiber and the matrix, swelling and shrinkage during moisture absorption, effect of osmotic pressure to propagate cracks along the fiber/matrix interface etc. Accelerated ageing has been used to obtain results on weathering performance of wood thermoplastic composites.

Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Infrared light can be categorized as far infrared ( $4\sim 400\text{cm}^{-1}$ ), mid infrared ( $400\sim 4,000\text{cm}^{-1}$ ) and near infrared ( $4,000\sim 14,000\text{cm}^{-1}$ ). Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. For example, the C = O stretch of a carbonyl group appears at around  $1700\text{ cm}^{-1}$  in variety of molecules. Hence, the correlation of the band wavenumber position with the chemical structure is used to identify a functional groups in a sample.

The objective of this study is to understand the effect of weathering on functional group and mechanical properties at the PP-kenaf composites and PP-kenaf-MAPP composites surface. Fourier transform infrared (FT-IR) spectroscopy was used to identify functional groups present at the surface of the composites. Measurement of mechanical properties was conducted by using tensile tester. Monitoring of mechanical properties including elastic modulus. The results of this study will be used to further research and development of kenaf-PP composite with improved weathering performance.

## EXPERIMENTAL METHOD

### Materials

The materials used in this study were kenaf fibers Grade C (short fiber) from PT GAN Malang. The kenaf fibers were ground into 60 mesh particle sizes and then

the kenaf flour was dried for 24 h at  $105^{\circ}\text{C}$ . The polymer matrix used in this study was polypropylene (PP, 60% weight basis, Union Polymer J 101 XX) and maleated anhydride polypropylene (MAPP, 1% weight basis, Toyo Kasegyo type M300 KS Japan) was used as compatibility agent to improve the tensile properties of PP-kenaf composites.

### Processing

The composites have been prepared from PP(60%w) + kenaf (40 %w) and PP(60%w) + kenaf (40 %w) + MAPP (1 %w); by *blending* method using laboplastomill mixer at  $175^{\circ}\text{C}$  for 8 minutes at 40 rpm, then the blend was pressed by using hotpress at  $175^{\circ}\text{C}$ , for 8 minutes with pressure of 50 kgf.

### Tensile Testing

Specimens were mounted into 100 kgf load cell of Universal Tensile Machine, Tensilon Orientec, type UCT-5T. Dumbell type used for specimen cutting is ISO 527 type 5A. One load cell statically fixed with the tensile machine frame and the second one fixed with the moveable part of the machine. Specimens were strained at displacement rate of  $1\text{ mm min}^{-1}$ . All specimens were deformed under controlled room condition at temperature of  $23 \pm 1^{\circ}\text{C}$  and humidity of  $50 \pm 5\%$ .

Dumbell specimens to be used for weathered and unweathered test. Samples for weathering tests were exposed to weathering. Weathering sampling periods is 5.5 month.

### Fourier Transform Infrared

Fourier transform infrared (FT-IR) spectroscopy was used to identify functional groups present at the surface of the composite surface before and after weathering. Samples analyzed include kenaf flours, commercial PP, commercial MAPP, weathered and unweathered PP-kenaf composites, weathered and unweathered PP-kenaf-MAPP composites.

About 0.08 mm slices were cut from the weathered and unweathered surface samples, then the sample crushed using liquid nitrogen and vacuum dried for 24 hours. Sample was mixed with KBr in a mortar and pressed into a transparent pellet. The FT-IR spectra were recorded on a shimadzu-4300 spectrophotometer in the  $4000\sim 400\text{ cm}^{-1}$  range. Spectrum were obtained at a resolution of  $4\text{ cm}^{-1}$  with total of 10 scan for each sample in absorbance mode.

Functional groups indices are commonly used for comparative purposes. The FT-IR lets characterize the chemical structure by identifying the functional groups present in each sample, then we compared typical bands for the composites to the kenaf fiber bands. In order to assign the absorbance of samples in spectrum,

we referred to the published data. The determination of functional group concentrations was thus limited to carboxylic acid and aldehydes groups. Therefore there is need to account for other carbonyl groups that are present and kenaf degradation in weathered composites. Thus, Carbonyl index (CI) and hydroxyl index (HI) were calculated as the ratio of the peak area (absorption) at 1800 to 1680  $\text{cm}^{-1}$  and at 3500-3080  $\text{cm}^{-1}$  [6] to a peak area that is chosen as a reference peak (least changed during blending and weathering )

## RESULTS AND DISCUSSION

Holia *et al.* have studied C class kenaf fiber as filler of polypropylene composites [3-5]. For PP-kenaf composites making, the blending temperature from 163 to 210°C is recommended. The thermal stability was decrease as the filler loading increased. PP-kenaf composites weathering result surfaces changes in color (Figure 1) and resulting in composites density reduction.

A series of FT-IR spectra for kenaf, PP, MAPP, unweathered PP-kenaf and PP-kenaf- MAPP composites were record in Figures 2(a) to 2(e). Carbonyl Index (CI) and Lignin Index (LI) of weathered and unweathered PP-kenaf and PP-kenaf-MAPP composites in comparison with kenaf fibers are shown in Table 1, while Hydroxyl Index (HI) and Moisture Index (MI) of its composites are shown in Table 2. Ratio of the peak areas at 1735 and 1715 to 2916  $\text{cm}^{-1}$  (A1735/A2916 and A1715/2916) were used to determine the CI, ratio of the peak areas at 1595 and 1505 to 2916  $\text{cm}^{-1}$  (A1595/A2916 and A1505/2916) for the LI , ratio of the peak areas at 3400 to 2916  $\text{cm}^{-1}$  for the HI, and bands observed in 1640  $\text{cm}^{-1}$  are



Figure 1. The surfaces of blending press PP-kenaf composite

Table 1. Carbonyl index ( CI) and lignin Index (LI) of weathered and unweathered PP-kenaf and PP-kenaf MAPP composites in comparison with kenaf fibers

Sample	CI		LI	
	A1735/A2916 (C=O)	A1715/A2916 (C=O)	A1595/A2916 (lignin)	A1505/A2916 (lignin)
PP/Kenaf composite weathered	0.112	0.096	0	0.008
PP-Kenaf MAPP composite weathered	0.081	0.079	0.005	0.005
PP-Kenaf composite unweathered	0.236	0	0.118	0.097
PP-Kenaf MAPP composite unweathered	0.221	0	0.116	0.105
Kenaf flours	0.905	0	0.432	0.311

attributed to the OH bending mode of water and the ratio peak areas at 1640 to 2916  $\text{cm}^{-1}$  can be used for an index of the MI. This peak (2916  $\text{cm}^{-1}$ ) was chosen as a reference peak because it changed the least during blending and weathering.

The spectrum of kenaf flour is presented in Figure 2 (a). The IR spectra contain the characteristic bands of celluloses. In the range of stretching vibrations of OH group there is a broad band (between 3200-3600  $\text{cm}^{-1}$ ) with a maximum peak around 3400  $\text{cm}^{-1}$  which is attributed to hydroxyl group stretching vibrations. The band at around 2900  $\text{cm}^{-1}$  is also strong which is associated with C-H stretching vibrations. A band at 1740  $\text{cm}^{-1}$  is associated with C = O stretching vibrations[7], it is indicative carboxyl groups in the xylan component of hemicellulose and also to chemical groups of lignin[8]. Bands at 1505 and at 1595  $\text{cm}^{-1}$  that are indicative of lignin [9], [10] and interpreted as guaiacyl-type lignins [11]. Peaks at around 1053  $\text{cm}^{-1}$  in a band regions (1003-1083  $\text{cm}^{-1}$ ) were assigned to C-O groups (combination of cellulose, hemicellulose and lignin) [12, 13]. A band in 1640  $\text{cm}^{-1}$

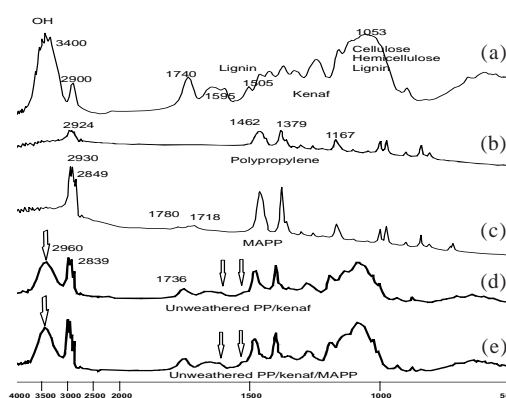


Figure 2. FT-IR spectra of (a). kenaf flour, (b). polypropylene, (c). MAPP, (d). PP/kenaf and (e). PP-kenaf-MAPP.

**Table 2.** Hydroxyl Index (HI) , Moisture Index (MI) and vinyl Index (VI) of weathered and unweathered PP-Kenaf and PP-Kenaf-MAPP composites

Samples name	HI	MI
	A3400/A2916 (OH stretching)	A1645/A2916 (H <sub>2</sub> O bending)
PP-Kenaf composite weathered	0.480	0.072
PP-Kenaf MAPP composite weathered	0.201	0.043
PP-Kenaf composite unweathered	0.861	0.153
PP-Kenaf MAPP composite unweathered	0.768	0.131
Kenaf flours	2.324	0.540

is attributed to the OH bending mode of water [14]. A small shoulder peak at 899 cm<sup>-1</sup> is indicative of cellulose β-1, 4 linked xylopyranose back bone anomeric carbon group frequency in cellulose and hemicellulose .

The FT-IR spectra of PP (Figure 2(b)) showed four distinct absorption bands. The bands at triplet peaks around 2924 cm<sup>-1</sup> are due to symmetrical and asymmetrical C-H stretching vibrations of CH<sub>2</sub> and CH<sub>3</sub> in the polyolefin chain, the absorbance bands from 1462 and 1379 cm<sup>-1</sup> are from C-H deformation vibrations of CH<sub>2</sub> and CH<sub>3</sub>, and the band at 1167 cm<sup>-1</sup> are associated with rocking vibrations of CH<sub>2</sub> and CH<sub>3</sub>, or C = C stretching vibrations from the polyolefin chain. The spectra of MAPP(Figure 2(c)) showed more little difference then the spectra of PP (Figure 2(b)). There are the small band near 1780 cm<sup>-1</sup> is attributed to anhydride C=O stretching. Bands found between 1720 and 1710 cm<sup>-1</sup> arise from C = O stretching vibrations in the MAPP [7].

FT-IR spectra PP-kenaf and PP-kenaf-MAPP composites in Figure 2 (d) and 2(e) confirmed the typical functional groups of kenaf and PP is still being in the blending composites. Peaks at around 3400 cm<sup>-1</sup>, 1595 cm<sup>-1</sup>, 1505 cm<sup>-1</sup> and 1053 cm<sup>-1</sup> are assigned to the kenaf component and peaks around at 1462 cm<sup>-1</sup> and 1377 cm<sup>-1</sup> are assigned to the PP component. Effect of blending on functional group of PP-kenaf and PP-kenaf-MAPP composites are decreasing of kenaf peaks at around 1595, 1505, 1647, and 1740 cm<sup>-1</sup> and showed absorption bands at peak 3400 cm<sup>-1</sup> decreased compared to kenaf particles. It is Indicating that there were less OH groups of the surface of samples. The curves in Figure 2(d) and 2(e) show that there is nearly no difference in the FT-IR spectra between PP-kenaf and PP-kenaf-MAPP composites which means that MAPP has little effect on chemistry composition of composites.

The results show that CI at 1715 cm<sup>-1</sup> increased (Table 1) while HI at 3340 cm<sup>-1</sup> decreased during weathering (Table 2). The decrease in HI indicated that

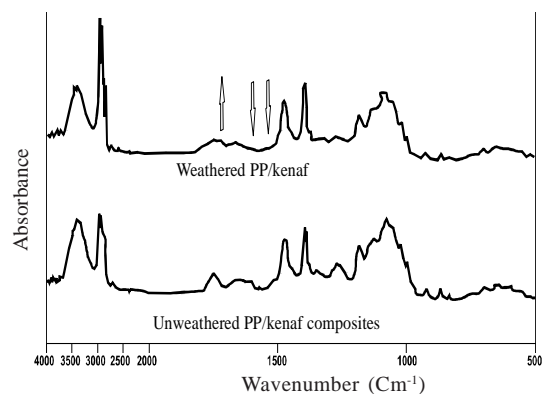
kenaf was lost during weathering. According to the MI values (Table 2), it can be concluded that moisture contents of PP-kenaf and PP-kenaf-MPP composites are lower than the kenaf fibers.

The results show that CI increased while HI decreased upon extended exposure time in weathering. The decreased in HI indicates that kenaf was lost upon extended exposure time during weathering.

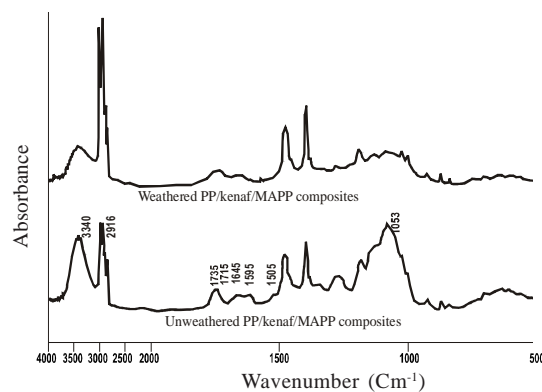
The PP-kenaf composites showed an increased intensity in peaks at 1462 and 1379 cm<sup>-1</sup>, although not clearly seen in Figure 2(d) and 2(e), which is indicative of the grafting reaction, suggesting more C-H character in PP-kenaf samples [7].

The PP-kenaf-MAPP composites (Figure 2 (e)), a distinct change was found near 2900 cm<sup>-1</sup>, where a large band near 2960 and 2839 cm<sup>-1</sup>, having distinct peaks similar in appearance to the maleated polyolefin, replaces the single peaks in the kenaf particle spectrum. This feature is characteristic of the maleated polyolefin (Figure 2(c)), and is due to C-H stretching vibrations. Another indication of grafting of the maleated polyolefin was an increased intensity in the band at around 1740 cm<sup>-1</sup>, possibly due esterification reaction, although not clearly seen in Figure 2 due to stacking of five in one figure.

FT-IR spectra of unweathered and weathered PP-kenaf composites were recorded in Figures 3 and



**Figure 3.** FT-IR spectra of (a). unweathered and (b). weathered PP-Kenaf composites



**Figure 4.** FTIR spectra of (a). unweathered and (b). weathered PP-Kenaf-MAPP composites



**Table 3.** Tensile strength, break strain and modulus of elasticity of weathered and unweathered PP-Kenaf /PP-kenaf MAPP composites

Sample	Tensile strength (MPa)	Break strain (%)	Modulus of elasticity (MPa)
PP	30.7±1.2	42	791±19
PP/Kenaf composite weathered	8.9 ±0.6	3.7 ±0.3	515.0 ±62.3
PP-Kenaf MAPP composite weathered	9.1 ±1.3	2.6 ±0.2	658.9 ±84.4
PP-Kenaf composite unweathered	13.0 ±4.2	1.5 ±0.4	1996.0 ±518
PP-Kenaf MAPP composite unweathered	14.9 ±1.4	1.0 ±0.3	2108.0 ±346

FT-IR spectra of unweathered and weathered PP-kenaf-MAPP composites were recorded in Figures 4.

Figure 3 shows FT-IR spectra obtained for PP-kenaf composites before and after weathering. The spectral features assigned to kenaf lignin assigned peak (1595 and 1505  $\text{cm}^{-1}$ ) decreased in intensity as a function of weathering time. The peak at wavenumber of 1505  $\text{cm}^{-1}$  corresponding to C=C stretching vibration in aromatic rings of lignin. The band at 1718  $\text{cm}^{-1}$  assigned to the carbonyl functional groups increased upon weathering.

Figure 4 shows FT-IR spectra obtained for PP-Kenaf-MAPP composites before and after weathering. The spectral features assigned to kenaf (C-O at 1015 to 1058  $\text{cm}^{-1}$  and OH at 3080 to 3500  $\text{cm}^{-1}$ ) regions decreased upon weathering. In addition, lignin assigned peak (1595 and 1505  $\text{cm}^{-1}$ ) decreased in intensity as a function of weathering time. Before weathering, the composites had the highest kenaf index. After weathering, the kenaf index of the composites decreased. The decrease in the kenaf index confirms a loss of kenaf at the composite surface [15]

The results show that the modulus of elasticity of unweathered PP-kenaf composites are higher but the tensile strength and the break strain are lower than PP. By adding 1% maleated anhydride Polypropylene (MAPP) in the blend, shows the increasing of tensile strength. Tensile strength and modulus of elasticity of composites decreased while break strain increased during weathering (Table 3). The reduction of mechanical properties was found to be due to degradation of lignin and PP chain scission as evaluated by increase in PP crystallinity after weathering [16].

## CONCLUSIONS

Kenaf fiber had complex function groups which include hydroxyl and carbonyl.

Surface chemical analysis of PP-kenaf and PP-kenaf-MAPP composites using Fourier transform infrared showed that lignin content decreased and surface oxidation (carbonyl content) increased during exposure. There is significant difference in weathering performance between PP-kenaf and PP-kenaf-MAPP composites, especially the decreasing of the tensile and modulus elasticity properties.

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