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EFFECT OF *CITRONELLA GRASS* FIBER ADDITION AND METHOD OF *CITRONELLA OIL* IMPREGNATION ON RICE STRAW-HIGH DENSITY POLYETHYLENE COMPOSITE

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ABSTRACT

Citronella grass and rice straw fiber with the size of 60 mesh were mixed and compounded with HPDE using twin screw extruder at compositions of 05:25:70, 10:20:70, 15:15:70 and 20:10:70 respectively. HDPE composites with same weight percent of polymer composition but different in fiber type loading were obtained. Rheological study was done and the result shows a slight increase in MFI value by the increase of *citronella grass* fiber loading. The new *Citronella Grass*/Rice Straw/HDPE composite (CGRSPE) were injected using injection molding into the test piece shape at the temperature around 140°C to 160°C. The study of tensile properties of CGRSPE composites was done. The results show the decreasing in tensile strength, Young's Modulus and elongation at break with the increase of *citronella grass* fiber loading. One of the compounded CGRSPE composite were selected and impregnated by citronella oil. The chemical constituent and thermal stability of the perfumed composites were studied.

Key Words: *Citronella grass*, *Citronella oil* rice straw, Natural fiber, Perfume impregnation

1.0 INTRODUCTION

Rice straw fiber can be considered as important potential reinforcing filler for thermoplastic composite because of its lignocellulosic characteristics. Global paddy production reached 628 million tons in 2005 with an additional 1% increase in 2006 [1]. Chemically, lignocellulosic rice straw fiber has similar compositions as other natural fibers used in thermoplastics. The whole rice straw fiber is composed of rice husk, leaf sheath, straw leaf blade, straw stem and knot, and straw root [2]. Various fiber components have different chemical constituents, especially cellulose and residual ash contents which contribute differently to the properties of rice straw fiber-reinforced thermoplastic composites.

Other than rice straw, *citronella grass* is also one of the lignocellulosic fiber that can be located easily in Malaysia. *Citronella grass* fibrous waste is normally been disposed to the landfill or used for animal feed after the oil content in the fiber has been extracted. These are the common practices adopted by extraction chemical industry in Malaysia. The essential oil from *citronella grass* is known as *citronella oil* which gives lime like fragrance. The oil has been traditionally used as anodyne, carminative, dentifrice, diaphoretic, disinfectant, insecticide, insect repellent, ruberfacient, stimulant, sudorific, soaps, fragrance and cosmetics. It also used as a folk remedy for chills, cholera, fever, headache, malaria, neuralgia, pain, rheumatism, stomach disorder, and thirst. In South Africa, they used as vermifuges, febrifuges and cold remedy [3].

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Previous study has been done to combine rice straw fiber with thermoplastic such as polyethylene. The obtained composite showed superior properties, and the extent of improvement in mechanical properties and dimensional stability of composites. However, there is no attempt in combining *citronella grass* with thermoplastic material. This is probably because of the low content of cellulose content of *citronella grass* fiber compared to rice straw fiber [2,4]. Therefore, the best solution is to mix both fiber together before combining it with thermoplastic polymer to overcome the weakness caused by low cellulose content of *citronella grass.*

2.0 MATERIALS AND METHODS

2.1 Materials

HDPE was used as the base resin in the composite compound. The resin was purchased from Polyethylene Malaysia Sdn. Bhd. with the brand name, Etilinas (HD5218AA). *Citronella grass* fiber was obtained from Serba Bagus Sdn. Bhd. and the rice straw fiber was obtained from Jarnuri Wastetech Sdn. Bhd. Ultra-Plast TP01 (dispersing agent) and Ultra-Plast TP10 (binding agent) were supplied by BASF (Malaysia) Sdn. Bhd. *Citronella oil* was provided by Chemical Engineering Pilot Plant (CEPP) UTM.

2.2 Formulation

Five types of formulations were compounded and tested including RSPE. The formulations were shown in Table 1.

Table 1 Raw material formulation and composition

Ingredients	**Weight, %**				
HDPE resin	70	70	70	70	70
Rice Straw	30	20	15	10	5
Citronella grass	0	10	15	20	25
Dispersing agent	1phr				
Binding Agent	1phr				

2.3 Sample Preparation

2.3.1 Drying Process

The rice straw and *citronella grass* powder obtained was maintained in dry condition prior to mixing process. HDPE resin was dried at temperature about 80°C for 2 hours prior to mixing and compounding. The drying condition was according to drier's manual instruction.

2.3.2 Dry Mixing Process

Mixing process was conducted in two phases. First, the rice straw powder and *citronella grass* powder were mixed using high speed mixing machine to ensure homogeneity between fillers. Then, the HDPE resin and the processing aid additive were added into mixed fillers. Every run took only 20-40 second to mix 3 kg materials at one time [5].

2.3.3 Compounding Process

Brabender Plasticorder model PL 2000 extruder was used to compound the dry mixed material into the uniform long strands. The temperatures that were maintained in three zones of the extruder barrel are 150, 160, and 175°C and the die temperature was set at 170°C. The screw speed was set to 50 rpm [5].

2.3.4 The Injection Molding

The compounded CGRSPE was injected into test sample at temperature from 140 to 165°C using JSW N100 BII Injection Molding unit completed with reciprocating screw type [5].

2.4 Method of *Citronella Oil* Impregnation

2.4.1 Normal Soaking Method

One of the formulations of the injected CGRSPE composite were selected and cut into pieces weight of 1.0g and then soaked in *citronella oil* for 2 hours. The ratio of *citronella oil* to CGRSPE composite is 10:1 in weight [6]. After 2 hours, the samples were taken out from the oil bed and dried at ambient temperature. The samples were then weighted several times until the weight become constant. The constant weight was then calculated using Equation 2.1 to determine percent in weight changes.

$$\text{Percent of weight change,\%} = \frac{\text{Final Weight (g)} - \text{Original Weight (g)}}{\text{Original Weight (g)}} \times 100 \qquad \textbf{(1)}$$

2.4.2 Pressurized Soaking Method

This method is a combination of normal soaking method which is the first method and high pressure method introduced by Hercules Inc. in 1985. The samples were soaked in a stainless steel tube at 4.5 bar using carbon dioxide for 2 hours as 4.5 bar is the highest pressure that can be detained by the equipment. All parameters and calculation method are similar to the normal soaking method.

2.5 Sample Testing

2.5.1 Fourier Transform Infrared (FTIR) Spectroscopy

All the raw materials and compunded composite were tested with KBr technique, using Perkin Elmer Spectrum I. The samples were scanned from 4000 cm^{-1} - 370 cm^{-1} for 16 times to reduce the noise to signal ratio.

2.5.2 Thermogravimetric Analysis (TGA)

Perkin Elmer Thermogravimetric Analyzer (TGA 7) was used to analyze the thermal stability of RSPE, CGRSPE and perfumed CGRSPE.in terms of the decomposition temperatures. The sample for TGA was heated from room temperature (30°C) to 750 °C at a heating rate of 20°C/min under nitrogen atmosphere [7].

2.5.3 Melt Flow Index (MFI) Measurements

The rheological analysis was done to study the flow behavior of the composite material using S.A. Associates Melt Flow Indexer in accordance with ASTM D 1238 procedures. According to the standard, load weighing 2.16 kg was applied at barrel temperature of 190°C.

2.5.4 Tensile Test

All compounded composite were cut according to ASTM D638. Using Instron Machine Model 5567, the crosshead speed was set to 50 mm/min.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of *Citronella Grass* Fiber on RSPE

3.1.1 Melt Flow Index (MFI) Measurements

From Table 2, the melt flow index (MFI) value for CGRSPE is increased by the increasing of *citronella grass* fiber content and the decrease of rice straw fiber content. The trend of changes of MFI values for all composites are shown in Figure 1. The decreasing of MFI value signifies the decrease of cellulose content in CGRSPE as the *citronella grass* fiber has lower cellulose content than rice straw fiber. *Citronella grass* fiber has a cellulose constituent of 28.5 % while rice straw fiber has 41-57% content of cellulose [2,4]. The value of MFI for RS:PE 30:70 is 4.393 and the value increase from 4.169 (CGRSPE 5:25:70) to 6.657 for CGRSPE 20:10:70. The MFI values for all composites were shown in Table 2.

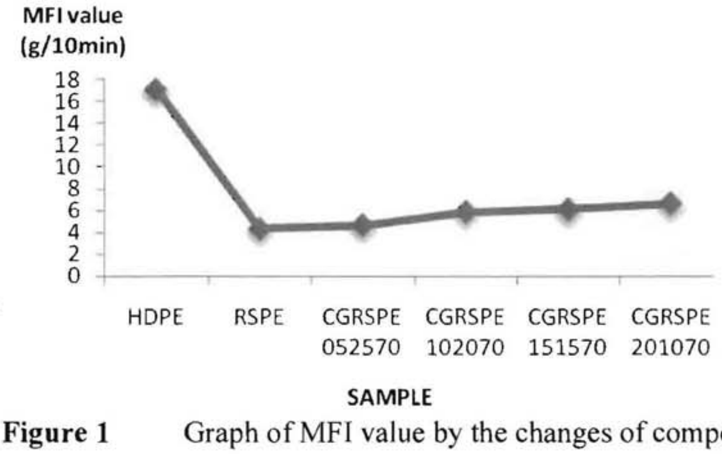

Figure 1 Graph of MFI value by the changes of composition.

Table 2 MFI value of samples.

Material	Composition	MFI value (g/10min)
HDPE (Virgin)	100	17.1
RS:PE	30:70	4.4
CG:RS:PE	5:25:70	4.6
CG:RS:PE	10:20:70	5.9
CG:RS:PE	15:15:70	6.1
CG:RS:PE	20:10:70	6.7

The increasing of the MFI value was due to the fact that cellulose which is the main reinforcing component in fiber, which is rice straw, is decreasing as the *citronella grass* fiber increased. The increased in the flow probably due to some oil still presence in the *citronella grass* fibers that can act as external lubricant. The different types of fiber may also cause the decrease of interaction between fibers and polymer chains as the structure of cellulose is different for each type of plant. Each type of cellulose has its own cell geometry and the geometry conditions determine the mechanical properties [8]. The increment in the MFI indicates good processablity. Thus addition of *citronella grass* fibers improved flows of the compound during processing.

However, the presence of rice straw and citronella fiber decrease the MFI value of composites compared to virgin HDPE which is 17.1. The low flow rate of RSPE and CGRSPE composites was probably due to the hindrance of the short fiber particles on the mobility of the HDPE matrix when the materials were forced to flow through the die. Nevertheless, because of the higher huge size of filler, the composites flowed at a lower rate [8]. *Citronella grass* fibers shows improvement in flow properties compared to rice straw alone.

3.1.2 Tensile Properties

Tensile strength, elongation at break and Young's Modulus of CGRSPE decrease as the content of *citronella grass* fiber increases. There was a slightly difference between the mechanical properties of CGRSPE as shown in Figure 2. The decrease of tensile strength could be due to the decreasing of interfacial adhesion resulting from the low cellulose content as shown in Figure 2 (a). Cellulose act as thus decrease the interfacial adhesion between chains. The *citronella oil* that is present in the *citronella grass* fiber probably is the main reason for the reduction in tensile strength since oils lubricate and act as plasticizer. The presence of plasticizer normally reduces tensile strength but improve impact properties.

There is small reduction in the elongation at break as the amount of *citronella grass* fiber composition is increased as shown in Figure 2 (b). The low interaction between polymer chain and fiber enhanced mobility of chains and made the polymers chains easier to slip. Less interfacial adhesion caused the chains to bind together with very low strength. Interaction between chains also decreased as the bond of polymer chain and fiber became lower. Therefore, the elongation of composites will become lower [9].

The decreased of tensile strength and the elongation at break results in the decline of Young's Modulus value for CGSPE composites. The Young's Modulus value for 5 wt% *Citronella grass* fiber is 1360.3 MPa and reduces to 1277.3 MPa for 20 wt% *citronella grass* fiber. The trend of changes of Young's Modulus can be seen in Figure 2 (c). The composite become less stiff as the *citronella grass* fiber content increase and the rice straw fiber decrease due to the plasticizing effect of oil content which is still presences in the *citronella grass* fibers. This indicates that *citronella oil* is not fully extracted from the fibers.

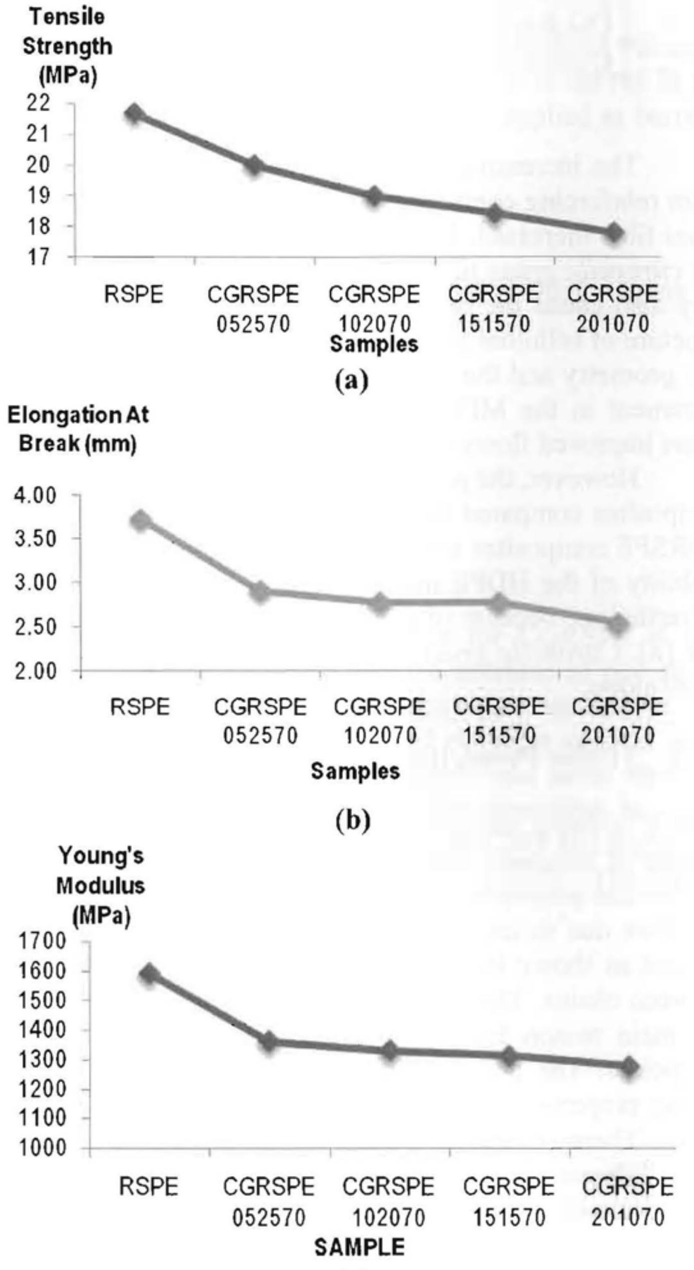

Figure 2 Mechanical properties of CGRSPE, (a) tensile strength, (b) Young Modulus and (c) Elongation at break

3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

From the Figure 3, the spectra of CGRSPE shows that the new composite has inherit all chemical constituent of its raw materials. The absorption at 3200cm^{-1} and 1650 cm^{-1} principally associated with absorbed water. There are more fine peak in citronella fiber between 1020-1500 cm^{-1} indicates ether, alcohol, ester and acid groups. This shows the presence of *citronella oil* in the citronella fiber and not all are being extracted during the extraction process. Figure 4 shows the *citronella oil* spectrum compared to *citronella grass* fiber. Both *citronella oil* and *citronella grass* fiber have similarity at peaks between 1020-1500 cm$^{-1.}$ The prominent band at 1050 is attributed to C-O, C-C stretching or C-OH bending in hemicelluloses [10]

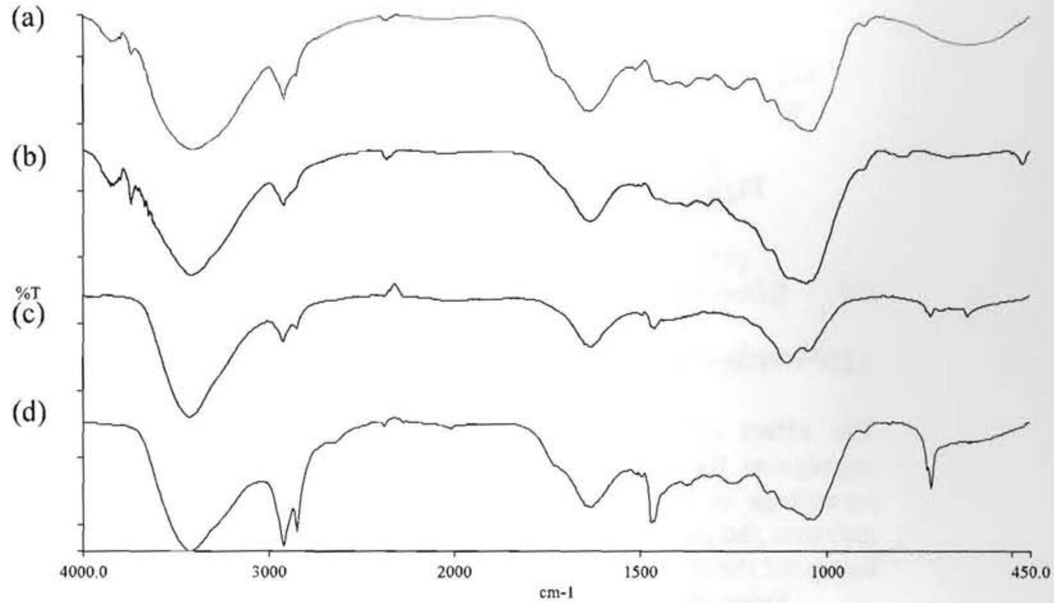

Figure 3 FTIR spectra of (a) citronella fiber, (b) rice straw fiber, (c) HDPE and (d) CGRSPE.

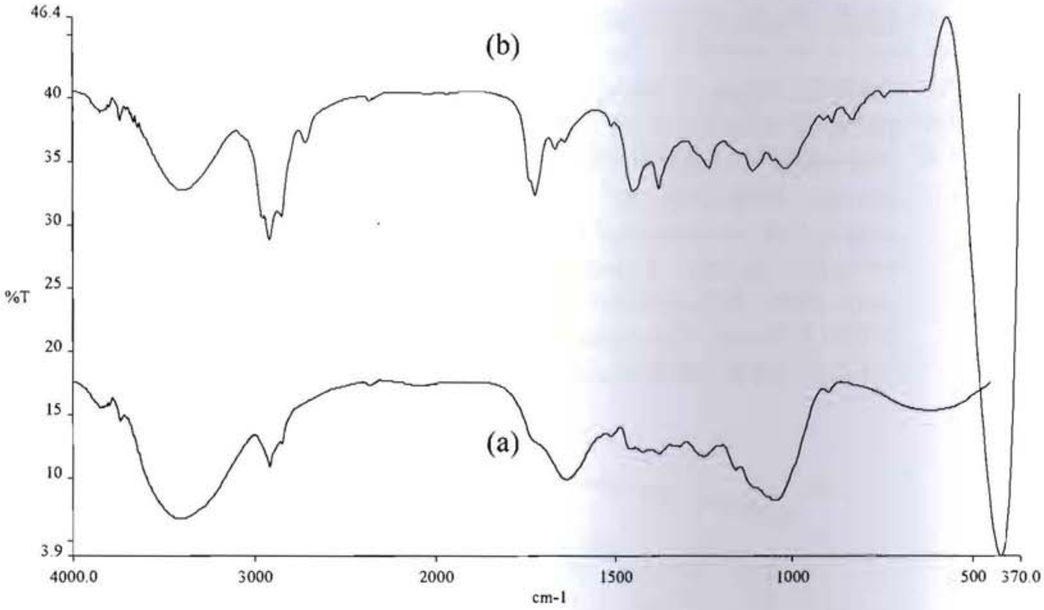

Figure 4 FTIR spectra of (a) citronella fiber and (b) citronella oil.

3.2 Effect of Method of *Citronella Oil* Impregnation to CGRSPE

3.2.1 Weight Change in CGRSPE (Oil Absorption)

The effect of using normal soaking method and pressurized soaking method to impregnate the CGRSPE composite with *citronella oil* was done by comparing the percentage of weight changes. The change of weight after the impregnation process indicates the performance of impregnation method. The oil absorbed by the composites increased the original weight of the composite.

From the Figure 5, the pressurized soaking method yield higher oil absorption with the weight change of 1.98%. The weight change for normal soaking method is only 0.17%. The difference of oil absorption between those two methods is quite big. Pressurized soaking method yield higher absorption because the ability of carbon dioxide gas to become transport medium for oil to travel into the polymer free volume. Carbon dioxide has low viscosity, near-zero surface tension, relative chemical inertness, and high diffusivity adsorption with guest molecules on the host substrate and therefore facilitates solute transfer relative to normal solvents [11]. The introduction of carbon dioxide increases the amount of oil absorbed into the composite.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Between the two methods of *citronella oil* impregnation, pressurized soaking method which gives higher oil absorption was selected and study for chemical constituent of the perfumed composite had been done. Comparing the FTIR spectra of RSPE, CGRSPE and *citronella oil* obtained from Chemical Engineering Pilot Plant (CEPP), UTM, CGRSPE inherit most of the constituent of citronella oil. From the result of FTIR in Figure 3.6, there are primary and secondary alcohol (1020/1100 cm^{-1}), aromatic ether

(1231 cm^{-1}), carboxylic acid (1231 cm^{-1}) and aldehyde (1723 cm^{-1}). *Citronella oil* contained borneol, capric acid, caprylic acid, carbone, citral, citronellal, citronellol, decanoic acid, euginol, formaldehyde, furfural, hydrocyanic acid, isoraleraldehyde, limonene, linalool, phellandrene, terpineol and vanillin [12]. Most of them are alcohols, carboxylic acids aldehydes which had been detected by FTIR spectra for both citronella grass/rice straw/polyethylene (CGRSPE) and citronella oil.

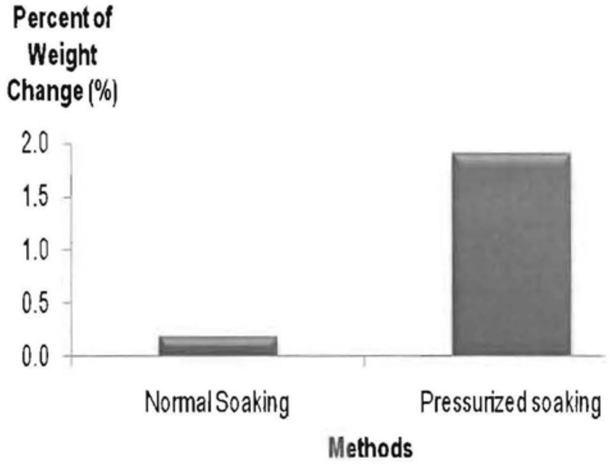

Figure 5 Weight Change in CGRSPE (Oil Absorption)

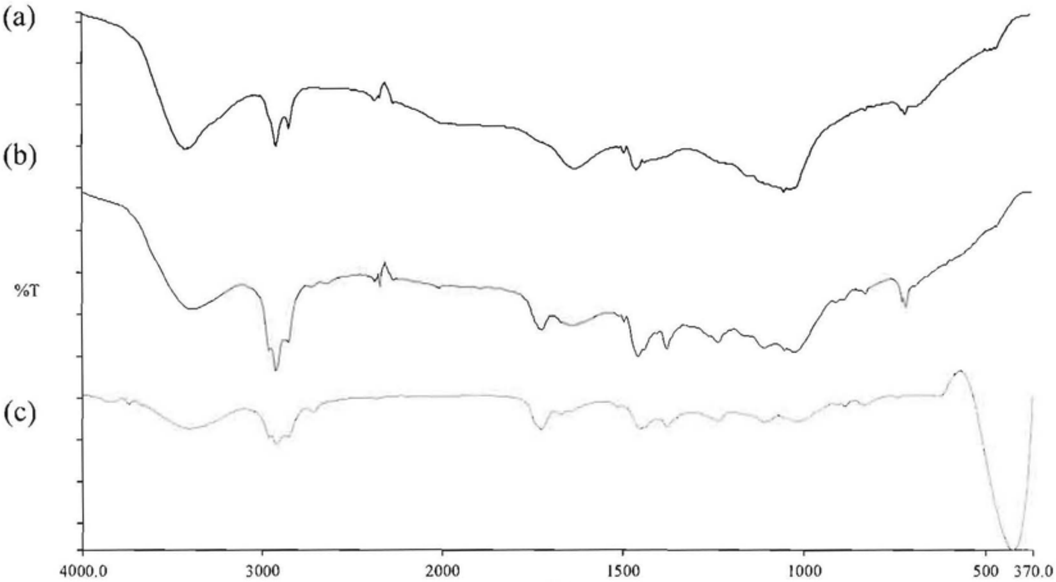

Figure 6 FTIR spectra of (a) CGRSPE, (b) Perfumed CGRSPE and (c) *Citronella oil.*

3.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to evaluate the degradation point of RSPE, CGRSPE and perfumed CGRSPE. The rate of weight loss of the sample as a function of temperature is measured to predict the thermal behavior of all three composites. The thermogravimetric behavior of RSPE, CGRSPE and perfumed CGRSPE in nitrogen atmosphere is shown in Figure 7.

There were three stages of degradation occuring to Perfumed CGRSPE compared to RSPE and CGRSPE composite which have two stages of degradation. The curve revealed an initial weight loss of the composite between 60-230°C. The loss indicates the elimination of *citronella oil* present in the *citronella grass* fiber component in CGRSPE s the *citronella oil* start to burn at 60°C [7].

The second slope of weight loss was between 230-360°C which is the same with the first stage of degradation of RSPE and CGRSPE. It must be due to the degradation of lignocellulosic material (rice straw and citronella grass) in the composite. This was followed by a slanting slope between 360-430 °C and a major weight loss starting at 430 °C, which ended by approximately 500-510 °C. The weight loss in this zone 370-510 °C was similar to the HDPE degradation behaviour. An amount of char remained after the rapid weight loss was believed to be from the degraded rice straw and citronella grass. Three major constituents of lignocellulosic materials (hemicellulose, cellulose, and lignin) are chemically active and decompose thermomechanically in the temperature range of 150-500°C (hemicellulose decomposes mainly between 150-350°C, cellulose decomposes between 275-350°C, and lignin undergoes gradual decomposition between 250-500°C [9,13].

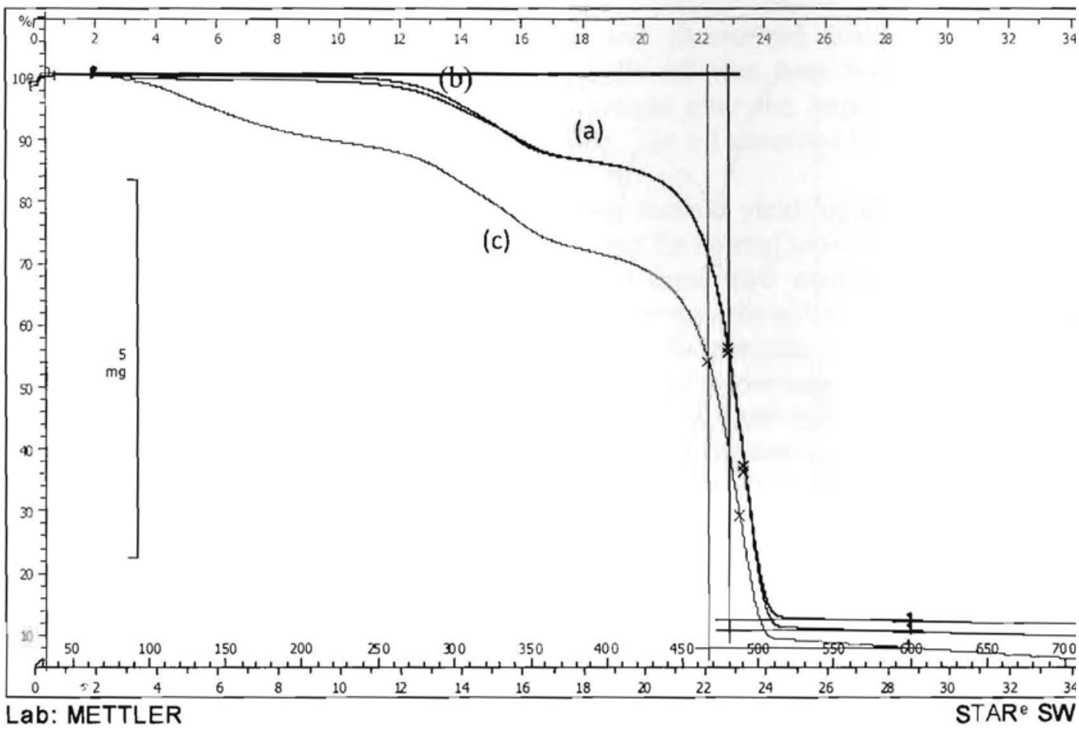

Figure 7 Thermogravimetric analysis of (a) RSPE, (b) CGRSPE and (c) Perfumed CGRSPE.

4.0 CONCLUSIONS

The study of the effect of *citronella grass* fiber on RSPE and methods of *citronella oil* impregnating CGRSPE had been done. Addition of *citronella grass* fiber into RSPE enhances the mobility of composite thus increase MFI value. However, tensile strength, elongation at break and Young's Modulus slightly decrease as *citronella grass* fiber composition increase and rice straw fiber decrease due to the plasticizing effect of the remaining *citronella oil* in the fiber. Cotronella fiber improved processability and also acts as plasticizer to the composite. Two method of *citronella oil* impregnation had been study and compared. Pressurized soaking method yield higher *citronella oil* absorption compared to normal soaking method. The perfumed CGRSPE show similar chemical constituent of combination of both *citronella oil* and CGRSPE and started to release volatile oil rapidly at temperature of 60°C.

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