

# Determination of Filler Content in Rice Husk Ash and Wood-Based Composites by Thermogravimetric Analysis

M. Y. AHMAD FUAD,<sup>1,\*</sup> M. J. ZAINI,<sup>1</sup> MUSTAFAH JAMALUDIN,<sup>1</sup> Z. A. MOHD ISHAK,<sup>2</sup>  
and A. K. MOHD OMAR<sup>2</sup>

<sup>1</sup>Plastics Technology Centre, Standards and Industrial Research Institute of Malaysia (SIRIM), P.O. Box 7035, 40911, Shah Alam, Malaysia; and <sup>2</sup>School of Industrial Technology, Universiti Sains Malaysia, 11800, Penang, Malaysia

## SYNOPSIS

Three new types of fillers for polypropylene are investigated. The first two were derived from burnt rice husk ash (RHA), whereas the third, a wood-based filler, was processed from oil palm trunk. One important characterization of the composites involves the checking for the actual filler content and filler distribution within the matrix. An analytical technique is described here for computation of the filler content in the composites based on a simple expression derives from thermogravimetric analyses. For filler with volatiles such as the black RHA, the derived expression was  $p_f = 106(r_b/m_c)$ , and for easily burnt fillers (wood-based), the expression was  $p_f = 156(m_d/m_c)$ . The technique has shown good agreement and consistency between analyzed and actual filler contents and a uniform filler distribution within the polypropylene matrix. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Fiber and particulate-filled polypropylene has never ceased to be a popular subject for many researchers working in various parts of the world.<sup>1-5</sup> Modifications of properties for polypropylene seems to be infinite with the introduction of apparently unlimited types of fillers. Mineral-based fillers such as glass fiber/spheres, calcium carbonate, mica, asbestos, silica, and Wollastonite are the more commonly used fillers, whereas organic fillers like wood flour, starch (for biodegradable plastics), and polyester fibers are gaining importance and have also been employed on an industrial scale. Use of reinforced polypropylene in electrical and automotive engineering has been increasing in recent years, mainly due to its excellent high modulus, which enables it to substitute for conventional materials in demanding engineering applications, particularly in the automotive sector.<sup>6</sup>

In the present study, methods for the determination of filler content in three types of polypro-

pylene composites are described. The first two use white and black rice husk ashes—which owe their origin from burnt rice husk ash (RHA)—as the incorporated fillers. Applications of white and black RHA as fillers in polypropylene have been described elsewhere.<sup>7</sup> Applications of RHA in structural concrete, cement, and lightweight building materials is also gaining popularity and have been described by several workers.<sup>8-10</sup> The third type of filler is a wood-based filler derived from the trunk of an oil palm tree (*Elaeis guineensis*), hence, the term oil palm wood flour (OPWF) filler. The applications of other wood-based fillers have been described by other workers.<sup>11-13</sup>

The fillers were incorporated into the polypropylene matrix by various means such as by a two-roll mill or through an extruder. Accurate filler loading and excellent filler dispersion were normally assumed. However, attempts were seldom made to support these assumptions scientifically. Filler losses during compounding or mixing processes and agglomeration of filler in the composites are not uncommon, thus the significance of the filler content and dispersion analyses.

For mineral-based fillers that can stand substantially higher temperatures than can the matrix material, the matter is easily resolved by burning off

\* To whom correspondence should be addressed.

the entire resin at a high enough temperature, leaving behind the inorganic filler for quantification. The glass fiber content of glass-reinforced plastics may be determined in this manner using a furnace up to say 600°C.

The thermogravimetric analytical technique gives a more precise control of the heating conditions such as variable temperature range, accurate heating rate, and choice of atmosphere (e.g., nitrogen, air, or oxygen). Only a small quantity of the sample is required for the analysis. The availability of highly sensitive microbalances and powerful data analysis software enable the computation of filler content to great precision and accuracy. The choice of atmosphere depends on the nature of the fillers; for inert inorganic fillers such as glass, talc, silica, and mica, flowing air or oxygen is preferred to virtually burn off the matrix materials. For organic fillers such as carbon black or black RHA in the polypropylene matrix, an inert nitrogen atmosphere will be more suitable so that only the matrix polypropylene will vaporizes through thermal degradation without affecting the carbon content significantly. If the matrix material does not completely volatilize and leaves behind some ash, then introduction of air is necessary at high enough temperature (550°C) to oxidize the carbon component and, thus, separating it from the ash for quantification purpose.<sup>14</sup> Applications of this technique for evaluating filler content have been described by many thermal analysts, but the scope of analyses were often limited to mineral fillers and carbon black determination.<sup>15,16</sup>

Content determination of filler with volatiles and wood-based filler using similar technique, however, poses a problem since the fillers themselves usually undergo mass loss due to volatiles or, in the case of the latter, the wood may degrade or carbonize even earlier than the matrix plastics. In this study, we report how filler content in such fillers may be calculated from simple expressions derived from selective thermogravimetric analyses. Filler contents of almost all the RHA and OPWF composites were conveniently determined with good accuracy and precision by these methods.

## EXPERIMENTAL

### Materials

The rice husk ashes (RHAs) were collected from open-air burning sites outside the mills. The poly-

propylene used was Propelinas 600G (homopolymer) from Polypropylene (M) Pte. Ltd. with density and melt index specified as 0.90 g/cm<sup>3</sup> and 12 g/10 min, respectively. The oil palm wood flour (OPWF) filler material of 125 μm particle size was obtained from Palm Oil Research Institute of Malaysia (PORIM). The polypropylene used was homopolymer WH 101 from The Polyolefin Company (TPC) with density and melt index specified as 0.90 g/cm<sup>3</sup> and 8 g/10 min, respectively. No coupling agent was used in the composites.

### Composites Samples Preparation

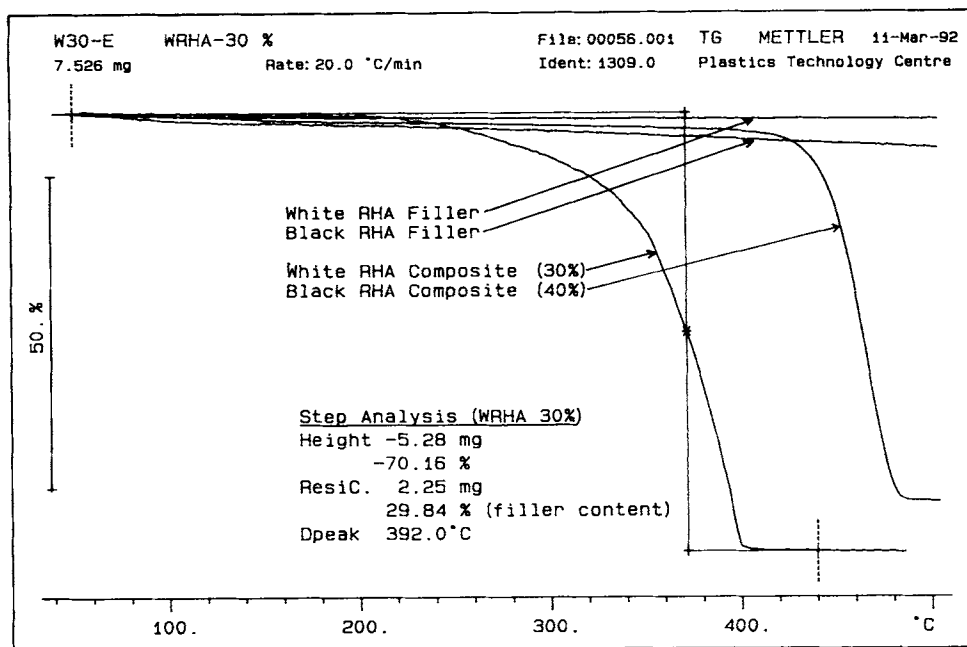
The fillers were compounded into polypropylene by means of a Brabender DSK 42/7 twin-screw compounder having barrel temperatures of 170–190°C from the feeding zone to the die zone, respectively. Four levels of loadings were prepared for all composites. The incorporated filler contents for white and black RHA composites were 10, 20, 30, and 40% (by weight). The OPWF composites were prepared by compounding 20, 30, 40, and 50 parts filler to 100 parts resin, resulting in a theoretical filler content (by mass) of 16.7, 23.1, 28.6, and 33.3%, respectively. The compositions and markings of the OPWF composites are as shown in Table I. The compounds were extruded through a twin 4-mm rod die into a water bath, then pulled and pelletized.

The compounded samples were prepared into test specimens by an injection-molding technique. The machine used was a 20-t Battenfeld BA 200 CD Plus machine, with a UNILOG 4000 control system (closed-loop control). A test specimen mold from Mastermold Inc. was employed to mold a rectangular (125 × 12.5 × 3.13 mm) test specimen to be used for thermogravimetric analyses.

**Table I Composite Samples Composition**

Composite Sample	OPWF Mass (phr)	Theoretical Filler Content by Mass (%)
OPC1	10.0	16.7
OPC2	20.0	23.1
OPC3	30.0	28.6
OPC4	40.0	33.3
OPCM*	—	50.0

\* Composite sample prepared by Brabender W50E mixer to countercheck apparent discrepancy in analyzed results of OPC4. Note that the sample was not injection molded.



**Figure 1** Thermogravimetric scans of white and black RHA fillers and their respective composites. Step analysis of white RHA composite (30% loading) gives direct filler content.

A highly filled OPWF composite at 50% filler content was also specially prepared using a Brabender W50E mixer to cross-check for an apparent discrepancy in the analyzed content of the OPC4 sample. Although all the previous samples were prepared by the twin-screw compounder and injection-molding process, this sample (OPCM) is prepared solely using a mixer with a 5 min mixing time. Mixing was performed by a pair of counter rotating rotors at a temperature of 180°C. Thermogravimetric analyses were performed on specimens taken from three different parts of the composite.

### Thermogravimetric Analysis

Filler content in the final samples was analyzed using a Mettler TG50 thermogravimetry analyzer with a TC11 TA Processor. The white RHA samples were scanned at a heating rate of 20°C/min from 50 to 550°C in *air* with a flow rate of 200 mL/min. The black RHA and neat polypropylene samples were scanned at a similar rate in an atmosphere of *nitrogen*. The RHA residue level was calculated using STEP analysis available in Mettler Graphware data evaluation software. Volatile loss from the RHA fillers has to be considered to ensure a more accurate computation of the filler content.

The OPWF composite sample was scanned in the

same conditions as those of black RHA, i.e., with a nitrogen purge gas. Great care has to be exercised in the analysis of the OPWF filler content as the filler degrades earlier than does the polypropylene matrix, as shown by the thermogravimetric scans in Figure 1. Although quite a substantial amount of degradation (carbonization) of the OPWF has occurred at 380°C, there seems to be hardly any significant degradation of the polypropylene matrix (as shown by the derivative thermogravimetric curve, DTG) up to this point. Thus, this temperature may serve as the upper limit of analysis in our subsequent computation for the OPWF content in the composites.

To check for filler distribution within the final composite samples, the filler contents were analyzed at three different positions within the bar specimen: at the gate, midpoint, and end positions of the bar.

### Filler Content Determination

#### White and Black RHA Composites

It has been shown in our previous publication<sup>17</sup> that in terms of the chemical composition the white RHA consists mainly of silica (96%) and other metal oxides make up the rest of the constituents. Black RHA, on the other hand, contains a high percentage

of carbon (48%), whereas silica remains to be the major constituent at 54% (Table II).<sup>18</sup>

Determination of filler content for white RHA composite is easy, as the white RHA is a thermally stable material and remains as the entire residue after all of the matrix polypropylene has volatilized off at 500°C. Direct STEP analysis of the white RHA composite scan will yield the filler content (Fig. 1).

Likewise, black RHA content may be determined easily when the sample was scanned in nitrogen. Oxidation of the carbon component will be suppressed by the inert nitrogen atmosphere content, thus leaving behind most of the filler as the residue. Careful thermogravimetric analysis of the neat black RHA filler, however, shows that even under the nitrogen atmosphere the filler itself undergoes loss of mass due to volatile loss. Hence, the residue does not represent the true quantity of the black RHA filler, the value of which will be significantly higher than initially calculated. Taking into account volatile loss, the actual filler content may be determined as follows:

If percentage volatile loss is  $p_v$ , then percentage filler residue at the end of the run,  $m_b$ , will be

$$m_b = 100 - p_v \quad (1)$$

If the mass of BRHA filler residue available after the scan is  $r_b$ , then the initial mass of the BRHA filler,  $m_i$ , present in the composite sample,  $m_c$ , may be determined as

$$m_i = 100r_b / (100 - p_v) \quad (2)$$

**Table II Chemical and Physical Properties of White and Black Rice Husk Ashes**

Property	White RHA	Black RHA
Chemical Composition/%		
CaO	0.1	0.1
MgO	0.4	0.2
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.0
K <sub>2</sub> O	1.6	1.1
Na <sub>2</sub> O	0.1	0.1
Al <sub>2</sub> O <sub>3</sub>	Trace	Trace
P <sub>2</sub> O <sub>5</sub>	Trace	Trace
SiO <sub>2</sub> (silica)	96.2	54.1
Loss on ignition (LOI)	1.6	44.5
Physical Properties		
Size/ $\mu$ m	5.4	2.4
Surface area (m <sup>2</sup> /g)	1.4	26.8
Density (g/cm <sup>3</sup> )	2.2	1.8

Percentage of BRHA filler present,  $p_f$ , in the composite sample,  $m_c$ , will then be

$$p_f = 100(100r_b) / m_c(100 - p_v) \quad (3)$$

Substituting for  $p_v = 5.6$  for the BRHA filler, then

$$p_f = 106r_b / m_c \quad (4)$$

In the general term, the expression may be written as

$$p_f = \bar{\omega}(r_b / m_c) \quad (5)$$

where  $p_f$  is the percentage filler content;  $r_b$ , the mass of the filler residue after the thermogravimetric scan;  $m_c$ , the mass of the composite sample in the thermogravimetric analysis; and  $\bar{\omega}$ , a constant related to the mass loss of the volatile in the filler.

### OPWF Composites

Step analysis of the neat OPWF thermogravimetric scan from 50 to 380°C shows a percentage mass drop of 62.6% (Fig. 2). If similar step analyses are carried out on the OPWF composites' samples within the above range, then the amount of filler present in each of the composites may be calculated. Within this temperature range, the polypropylene matrix degradation process has hardly commenced yet and the mass loss is probably due to volatiles. For better accuracy, mass loss due to these volatiles shall be taken into account as well.

Between the 50 and 380°C temperature range, it may be observed that there is a loss of 2.4% in case of the neat polypropylene (Fig. 2). If the mass drop of the composite sample is  $m_d$ , then the polypropylene (percentage) contribution to the loss,  $m_p$ , may be expressed as

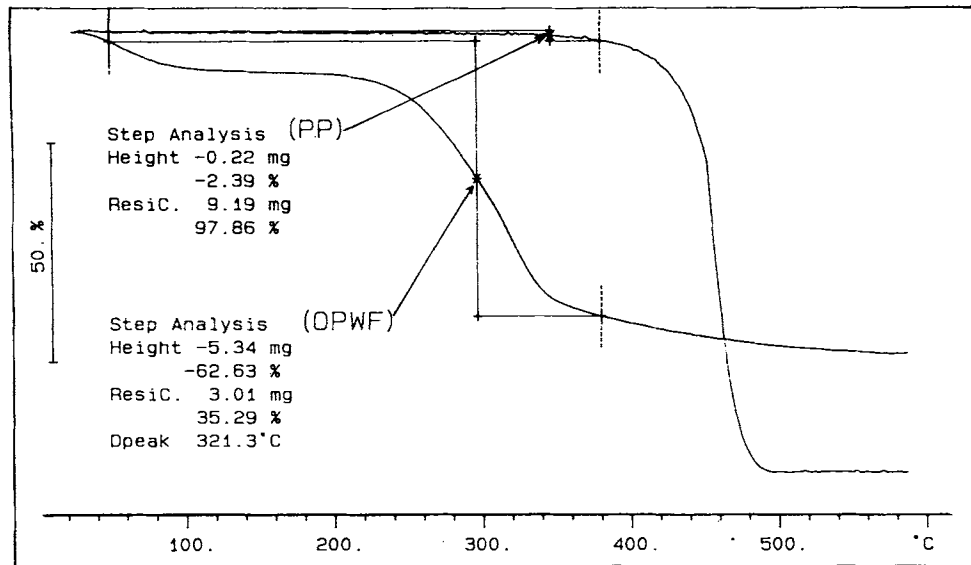
$$m_p = m_d(2.4/100) \quad (6)$$

Loss in mass due to filler only, i.e.,  $m_f$  will be

$$m_f = m_d - m_p \quad (7)$$

Since within the temperature range of interest the percentage mass drop was 62.6, then the initial mass of filler in the sample,  $m_f$ , will be

$$m_f = m_f'(100/62.6) \quad (8)$$



**Figure 2** Step analyses of thermogravimetric scans of neat polypropylene and OPWF between 50°C and 380°C. Note the mass loss of 2.4% for the polypropylene and 62.6% for the OPWF filler within the temperature range.

Substituting the value of  $m_f$  in eq. (8) will give the corrected filler content:

$$m_f = 1.56m_d \quad (9)$$

Percentage filler content in the OPWF composites,  $p_f$  (after correction has been made to account for the polypropylene mass loss within the temperature range analyzed) will be

$$p_f = 100m_f/m_c \quad (10)$$

$$p_f = 156(m_d/m_c) \quad (11)$$

In general terms, eq. (11) may be expressed as

$$p_f = \Psi(m_d/m_c) \quad (12)$$

**Table III Filler Content of Composites (40% Loading) at Different Locations in an Injected Sample Showing Good Filler Distribution**

Sample	Theoretical Filler Content (%)	Measured Filler Content (%)		
		Position of Sampling		
		Gate	Midpoint	End
White RHA	40.0	39.4	39.6	38.8
Black RHA	40.0	39.7	40.0	40.1

where  $\Psi$  is a constant related to the mass losses of the filler and the matrix materials when subjected to a specified range of a temperature profile.

To check for filler distribution within the final composite samples, the filler contents were analyzed at three different positions within the bar specimen. If the values are close to each other, they give a good indication of uniform filler dispersion within the matrix.

## RESULTS AND DISCUSSION

The thermogravimetry technique was used to study the filler content and distribution within the final composites. The analyses reveal that the determined filler content in both white and black RHA composites are very close to the percentage of the incorporated fillers, as shown in Table III. The thermogravimetry analyses also confirm excellent macroscopic distribution of filler particles within the matrix as filler contents at three different locations of the specimen (at the gate, midway, and end position away from injection gate) show very close agreement (Table IV).

White RHA samples were analyzed in air to burn off the polypropylene matrix, the residue being white RHA, which consists predominantly of silica. Black RHA samples were analyzed in oxygen-free nitrogen

**Table IV Analyzed Filler Content in RHA Composites as Determined by Thermogravimetry Analysis**

Theoretical Filler Content/%	Analyzed Filler Content (%)	
	White RHA	Black RHA
10.0	10.4	10.5
20.0	18.4	20.5
30.0	29.9	29.5
40.0	38.8	39.9

(OFN) to burn off the polypropylene matrix but without oxidizing the carbon content of the RHA.

Results for the analyzed OPWF contents in the composites are shown in Table V. The analyses reveal that the determined filler contents in all the OPWF composites (exception: OPC4 sample) are quite close to the percentage of the incorporated fillers. As expected, the mean filler contents of samples OPC1, OPC2, and OPC3 are slightly lower than the theoretical values due to filler losses during the compounding process. The sample with the highest filler loading, OPC4, however, when analyzed gives a considerably lower value. This discrepancy may be attributed to higher filler losses relative to former samples. It was observed during the compounding process, at too high a filler content, that the mixing process became less efficient, i.e., greater difficulty was encountered to incorporate the filler. As feeding of the filler and resin was assisted by a dozing screw

feeder, occasionally at the earlier stage of compounding, a higher proportion of the resin (than the filler) tends to be fed into the compounder. Hence, this discrepancy may be attributed to inefficient mixing and not due to shortcomings in the analyzing technique.

To cross-check for this matter, a highly filled composite (50% filler content) was specially prepared using an alternate processing technique, i.e., by a mixer. The analyzed filler contents of this sample (OPCM) taken at the three different locations give good agreement to the theoretical value as shown in the last line of Table V. The mean value of 47.4% may be considered quite close, considering the inevitable filler losses during mixing process.

The uniform distribution of filler particles within the matrix in all the composite samples was also confirmed by the thermogravimetric analyses. Filler contents at three different locations of the specimen (at the gate, midway, and end position away from injection gate) were in close agreement to one another. The standard deviation value for each sample was also noted to be small. A typical plot of thermogravimetry scans for OPWF composites at various filler loadings is shown in Figure 3.

## CONCLUSION

Different methods for calculating the filler contents of three types of fillers have been described. First, for thermally stable fillers such as the white RHA and other mineral fillers, the residue at the end of a thermogravimetric scan represents the filler con-

**Table V Filler Content of OPWF Composites at Different Locations**

Composite Sample	Theoretical Filler Content (%)	Measured Filler Content (%)			
		Position of Sampling			
		Gate	Midpoint	End	Mean
OPC1	16.7	17.6	15.6	16.6	16.5 ± 0.8*
OPC2	23.1	21.2	22.6	22.0	21.9 ± 0.7
OPC3	28.6	25.7	25.3	25.6	25.5 ± 0.2
OPC4	33.3	27.4	28.5	27.3	27.7 ± 0.7
		Position 1	Position 2	Position 3	
OPCM	50.0	46.8	48.3	47.1	47.4 ± 0.8

\* Standard deviation.

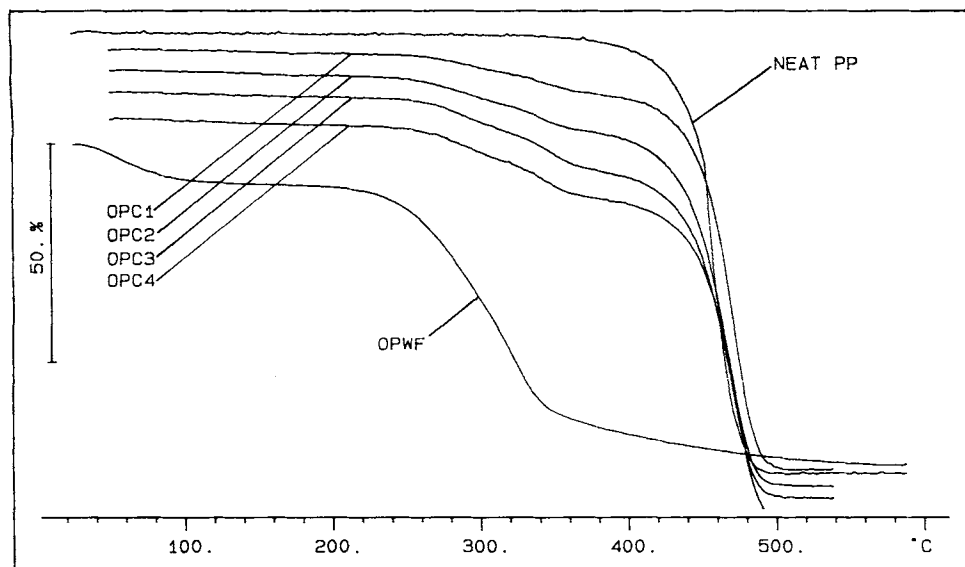


Figure 3 Thermogravimetric scans of OPWF composites with increasing filler contents.

tent. Second, for fillers that experience volatile losses such as the black RHA, the derived expression  $p_f = \bar{\omega}(r_b/m_c)$  is applied.  $\bar{\omega}$  is a constant that equals 106 in the case of the black RHA filler and  $r_b$  is the mass of residue at the end of the thermogravimetric run.

The final method is more intricate since it deals with wood-based fillers, which themselves undergo thermal degradation together or even prior to the matrix material. Another expression,  $p_f = \Psi(m_d/m_c)$ , has been derived to assist filler content computation of such fillers. The constant  $\Psi$  relates to mass losses of both filler and matrix materials when the composite sample is subjected to a specified range of a temperature profile in the thermogravimetric scan.  $\Psi$  equals to 156 for our oil palm wood flour/polypropylene system and it varies according to the type of wood-based fillers and matrix materials used.  $m_d$  is mass loss over the temperature range, whereas  $m_c$  is the initial mass of the composite sample analyzed.

Based on the described methods and expressions above, it was found that good agreement and consistency exist between the analyzed filler content and the theoretical incorporated values for all the composite systems investigated. This provides strong evidence to support the reliability of the described methods. The derived expressions provide a simple method for calculating the filler content of thermally unstable fillers. The expressions will enable research workers to have a quick and convenient means of checking the actual filler contents of their

composites and its dispersion within the matrix after spending a few laborious filler-compounding days in the laboratory.

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## REFERENCES

1. L. Jilken, G. Malhammar, and R. Selden, *Polym. Test.*, **10**, 329 (1991).
2. J. W. Ess and P. R. Hornsby, *Plast. Rubber Process. Appl.*, **8**, 147 (1987).
3. A. M. Riley, C. D. Paynter, P. M. McGenity, and J. M. Adams, *Plast. Rubber Process. Appl.*, **14**, 85 (1990).
4. L. E. Nielsen, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 1897 (1979).
5. D. M. Bigg, *Polym. Compos.*, **8**, 115 (1987).
6. A. Weber, *Plast. Rubber Process. Appl.*, **14**, 65 (1990).
7. M. Y. A. Fuad, J. Mustafah, Z. A. M. Ishak, and A. K. M. Omar, *Int. J. Polym. Mater.*, **19**, 75 (1993).
8. H. Mahmud, in *Proceedings of the Fourth JSPS/BCC Seminar on Integrated Engineering*, Kyoto, Japan, Oct. 1992.
9. M. Ramli, in *Proceedings of the Sixth Congress and Seminar on Science and Technology*, Kuala Lumpur, Malaysia, Aug. 1992.

10. B. P. Chang, in *Proceedings of Regional Seminar on Management and Utilization of Agricultural and Industrial Waste*, UNESCO-University Malaya joint seminar, Kuala Lumpur, Malaysia, March 1990.
11. S. N. Maiti and R. Subbarao, *Int. J. Polym. Mater.*, **15**, 1 (1991).
12. R. G. Raj, B. V. Kokta, G. Groleau, and C. Daneaut, *Plast. Rubber Process. Appl.*, **11**, 215 (1989).
13. M. G. S. Yap, Y. T. Que, L. H. L. Chia, and H. S. O. Chan, *J. Appl. Polym. Sci.*, **43**, 2057 (1991).
14. J. J. Maurer, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, San Diego, 1981, p. 572.
15. B. Cassel, in *Proceedings of the Sixth North American Thermal Analysis Society Conference*, Princeton, NJ, 1976.
16. G. Widmann and R. Reisen, in *Thermal Analysis—Terms, Methods, Applications*, Huthig, Germany, 1987, p. 113.
17. M. Y. A. Fuad, R. Shukor, Z. A. M. Ishak, and A. K. M. Omar, *Plast. Rubber Comp. Process. Appl.*, to appear.
18. M. Y. A. Fuad, O. Salleh, Z. A. M. Ishak, and A. K. M. Omar, *ASEAN J. Sci. Technol. Dev.*, to appear.

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