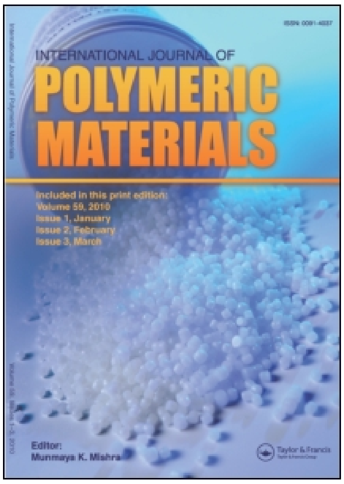

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RICE HUSK ASH AS FILLER IN UNSATURATED POLYESTER BASED SHEET MOULDING COMPOUNDS (SMC)

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Sheet moulding compounds were made from unsaturated polyester resin as matrix material filled with calcium carbonate, white rice husk ash and black rice husk ash. The objective of this investigation was to utilize the white and black rice husk ash, which are available in large quantities and which pose environmental problems in rice-producing areas. The investigation showed that black ash has a profound effect to increase the modulus of rupture, modulus of elasticity, as well as to reduce the thickness swelling and water absorption. Scanning electron microscopic studies showed that the black ash retained the fibrous morphology and thus has a better reinforcing function than white ash, which is amorphous. Reduction in water absorption and thickness swelling should be attributed to the hydrophobic nature of carbonaceous residues present on the outer surface of black ash. Formation of organosilicon compounds during the processing of the black ash was at first suspected to be responsible for the water repellency; but the ^{29}*Si MAS NMR studies did not provide evidence for the formation of such compounds.*

Keywords: rice husk ash, sheet moulding compounds (SMC), mixture design, SEM studies, resin matrix, unsaturated polyester resin

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INTRODUCTION

A huge quantity of waste in the form of rice husk is created worldwide by the rice milling process. In many locations rice husks are disposed of by dumping or open burning. Rice husk when burnt in open air outside the rice mills yields two types of rice husk ashes (RHA) that have good potential to serve as fillers [1]. The upper layer of the RHA mound is subjected to open burning in air and yields black carbonized ash. The inner layer of the mound being subjected to a higher temperature profile results in complete oxidation of carbonized ash to yield white ash that consists predominantly of silica.

Black RHA may also be obtained from burners where rice husk has been burnt for a short duration of time as a fuel.

The use of rice husk ash in non-polymeric products has been extensively studied and reported [2–4]. Examples of other applications include synthesis of zeolite [5–6] and as filler in building materials. Extensive work has been carried out by Fuad and co-workers [1–2, 7–8] on the use of rice husk ash as filler in polypropylene.

In the present work both the white and black rice husk ashes were employed as filler along with calcium carbonate in the preparation of sheet moulding compounds (SMC). SMC-process is one of the important process technologies for fiber reinforced polymers today. It is characterized by the flow behavior of the semi-finished flat SMC-sheet under heat and pressure in the press mould. The SMC sheet is built up continuously from short fiber (20–50 mm) or endless fiber mats impregnated with a filled resin system. Calcium carbonate is the filler very widely used in the unsaturated polyester resins for the production of SMC. The reactive monomer in the unsaturated polyester is normally styrene. The objective of the present studies was to determine the effect of black and white ash on the physical and mechanical properties of the moulded composites. For this purpose "statistical experimental design with mixture" was employed for collecting and analyzing the data.

EXPERIMENTAL

Materials

Calcium carbonate filler used in the present work was Omyacarb obtained from Omya Southern PTY, Adelaide, Australia. Black rice husk ash (with mean particle size 20 μm) and white rice husk ash (with mean particle size of 13 μm) obtained from Bernas (M) Sdn. Bhd., Anak Bukit Alor Setar, Kedah Darulaman, Malaysia. Unsaturated polyester resin was the General Purpose, Orthophthalate type with styrene as reactive diluent obtained from Rivertex, Johor Baru. Chopped strand mat made from 1″E-Glass was obtained from Europharma.

Methods

For the determination of the composition of black and white rice husk ash X-ray fluorescence (XRF) measurements were carried out using the spectrometer Spectra plus of Bruker Analytical X-ray systems. Table 1 gives the composition of the rice husk ash.

The Scanning Electron Microscopic studies were performed in Jeol JSM-6600 Scanning Microscope. The particles of rice husk ash were metallized with gold (about 50 nm) in a sputter device (Balzers-Union) using Ar as sputter gas.

Preparation of Matrix Material for SMC

The quantities of individual fillers were decided based on "mixture design" (described under the Experimental Design section). The composition of the filler mixtures for the various experiments are given in Table 2. The other ingredients needed for blending were unsaturated polyester resins, thickening agent (MgO), internal mould releasing agent (zinc stearate), and latent catalyst (tert-butyl perbenzoate). All these ingredients were mixed according to the following general formulation: Unsaturated polyester, 100 parts; fillers (variable according to experimental design of Table 1); tert-butyl perbenzoate, 4 parts; zinc stearate, 1 part; MgO, 2 parts.

Fillers were added to the resin with vigorous stirring until they were uniformly dispersed free from lumps. Tertiary butyl perbenzoate

TABLE 1 X-ray Fluorescence (XRF) Analysis of White Rice Ash and Black Rice Ash

Composition	White Rice ash	Black rice ash
Na_2O	0.016	0.013
Mg O	0.490	0.228
Al_2O_3	0.020	0.020
Si O_2	94.92	38.080
P_2O_5	0.908	0.413
K_2 O	2.098	1.481
Ca O	0.770	0.177
Ti O_2	0.007	0.002
MnO	0.157	0.025
Fe_2 O_3	0.080	0.050

TABLE 2 D-Optimal Mixture Design—Experimental Points, Physical and Mechanical Properties of the Composites

Run No.	Factor A: WRHA	Factor B: BRHA	Factor C: $CaCo_3$	M.O.E. N/mm^2	M.O.R. N/mm^2	Water Abs.%	Thickness Swelling %
1	0.2	0.2	0.6	614.9	101.23	2.623	3.432
2	0.2	0.2	0.6	782	118.65	2.202	2.044
3	0.2	0.08	0.72	550.72	141.96	2.892	3.127
4	0.08	0.2	0.72	1255.46	135.58	1.721	1.854
5	0.12	0.08	0.8	674.62	124.42	2.202	3.066
6	0.08	0.12	0.8	814.11	145.50	1.798	2.948
7	0.18	0.08	0.74	586.26	111.17	2.936	4.818
8	0.08	0.16	0.76	761.00	127.29	1.748	2.304
9	0.2	0.14	0.66	825.41	104.71	1.647	2.483
10	0.14	0.2	0.66	1342.42	115.11	1.536	2.074
11	0.14	0.14	0.72	.82801	96.99	1.711	2.462
12	0.2	0.2	0.6	619.61	101.02	2.571	3.72
13	0.2	0.2	0.6	788.90	120.65	2.166	2.028
14	0.2	0.08	0.72	545.99	137.05	2.722	3.001
15	0.08	0.2	0.72	1276.76	131.56	1.63	1.852
16	0.12	0.08	0.8	669.55	120.50	2.226	3.201
17	0.08	0.12	0.8	811.31	131.36	1.75	2.886
18	0.18	0.08	0.74	591.38	112.36	2.769	4.338
19	0.08	0.16	0.76	762.35	134.65	1.634	2.5
20	0.2	0.14	0.66	824.38	104.06	1.533	2.494
21	0.15	0.19	0.66	1345.22	121.00	1.529	2.237
22	0.14	0.14	0.72	830.51	96.00	1.626	2.491

was added to the mix followed by zinc stearate and finally magnesium oxide.

Preparation and Moulding of SMC

The mixture of resin and fillers (matrix material) as prepared in the previous section was coated on two high-density polyethylene films. The quantity of the matrix material was such that glass fiber constitutes 25% of the final SMC. The fiber glass chopped strand mat was sandwiched between the two coated films and the resin was allowed to impregnate the mat intimately by rollers. The SMC mat so formed was covered by cellophane film to prevent loss of styrene and was allowed to thicken to leathery consistency to obtain a tack-free sheet moulding compound.

The SMC was moulded in a closed mould in a compression moulding press at 140–150°C at a pressure of 12 Kg/cm^2 for 5 min to get a cured composite of 4 mm thickness.

Experimental Design

Statistical "Mixture Design" was used for carrying out the entire experimentation. A mixture experiment is a special type of response surface experiment in which factors are the percentage or weight fraction or mole fraction of the ingredients of a mixture and the response is a function of the proportions of each ingredient. The problem of associating the measured properties (physical characteristics) of such mixtures with the ingredient composition centers around the determination of a suitable mathematical equation that adequately fits the experimental response [9]. One of the desirable characteristics of the experimental design is that experimental points are spread throughout the design region and from which a suitable mathematical model with minimum variance of the coefficients can be obtained [10]. Such a design has been reported to be provided by the "D-Optimal point selection" available from software "Design-Expert-5" of Stat-Ease Inc. [Stat-Ease, Inc., 2021 E. Hennepin Ave., Suite 480, Minneapolis, MN 55413-2726, USA].

Three filler types were used in the series of experiments: (1) White rice husk ash; (2) black rice husk ash; and (3) calcium carbonate. Unrestricted variation in the proportions of these fillers was not possible because certain compositions resulted in a viscosity too high to be of practical feasibility. Such a composition constitutes an invalid mixture. Variable composition could be achieved only when constraints were imposed on the composition. After a number of preliminary trials the following constraints on the composition (weight fraction) could be determined:

$$0.6 \leq CaCO_3, \leq 0.8$$
$$0.075 \leq \text{WRHA} \leq 0.2$$
$$0.075 \leq \text{BRHA} \leq 0.2$$

On the basis of these constraints the experimental mixture compositions as given in Table 2 were adopted.

Determination of Physical and Mechanical Properties of the Moulded SMC

The following ASTM methods were employed for the determination of the relevant properties indicated against each method:

ASTM D—256-81 Impact strength
ASTM D—570-77 Water absorption
ASTM D—790-80 Bending properties

RESULTS AND DISCUSSION

Chemical and Microscopic Examination of White and Black Ash

The composition of the white ash and the black ash samples are given in Table 1. From the Table it can be observed that the white ash predominantly contains silica whereas the black ash contains much less silica but predominantly carbon (58.51% by difference). The SEM photographs of the white and black ash samples that are used in the matrix material are given in Figures 1 to 3. It can be seen that the white ash particles are amorphous in character whereas the black ash particles retain the fibrous structure.

Effect of Composition of the Fillers on the Physical and Mechanical Properties

The various physical and mechanical properties of the moulded SMC samples made under a wide range of compositions were determined. These results are tabulated in Table 2.

The response equations relating the compositional variables and the relevant properties were determined from these results. Different

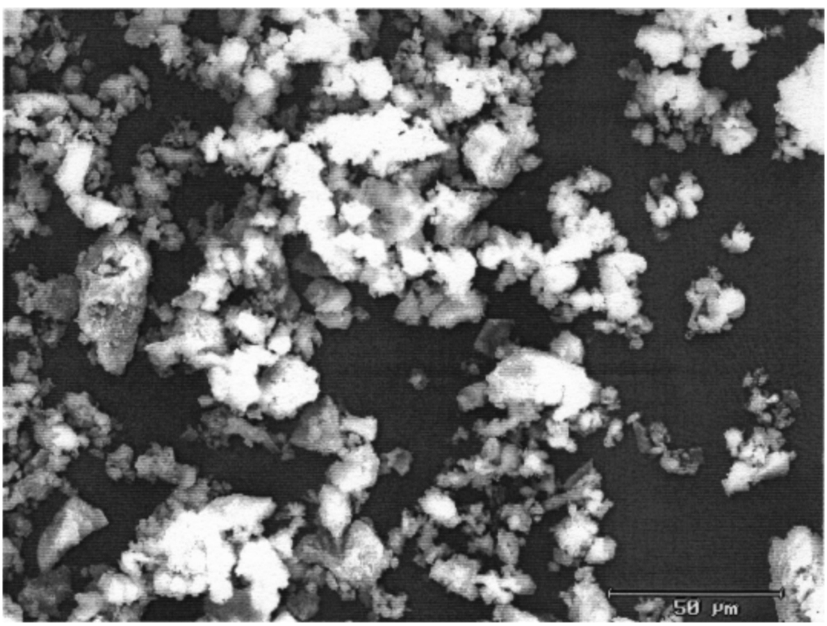

FIGURE 1 SEM photographs of white ash.

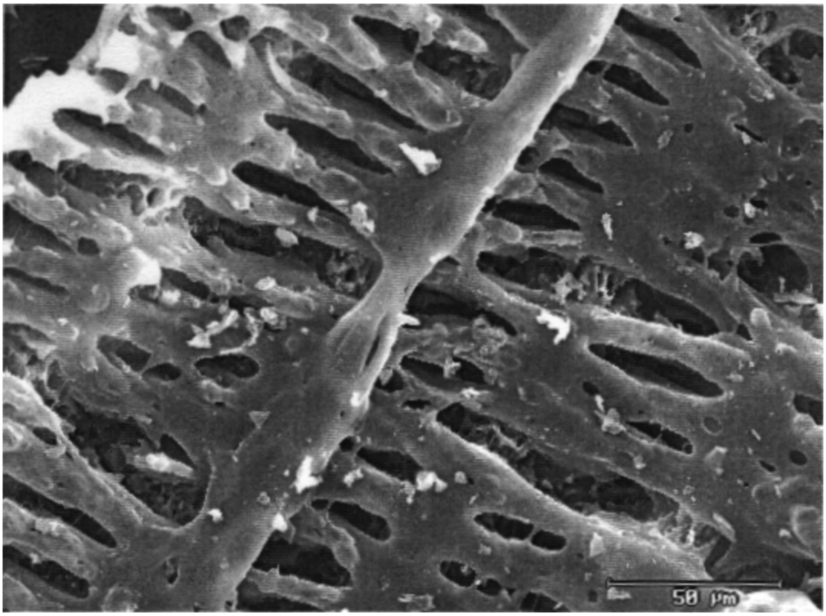

FIGURE 2 SEM photographs of black ash.

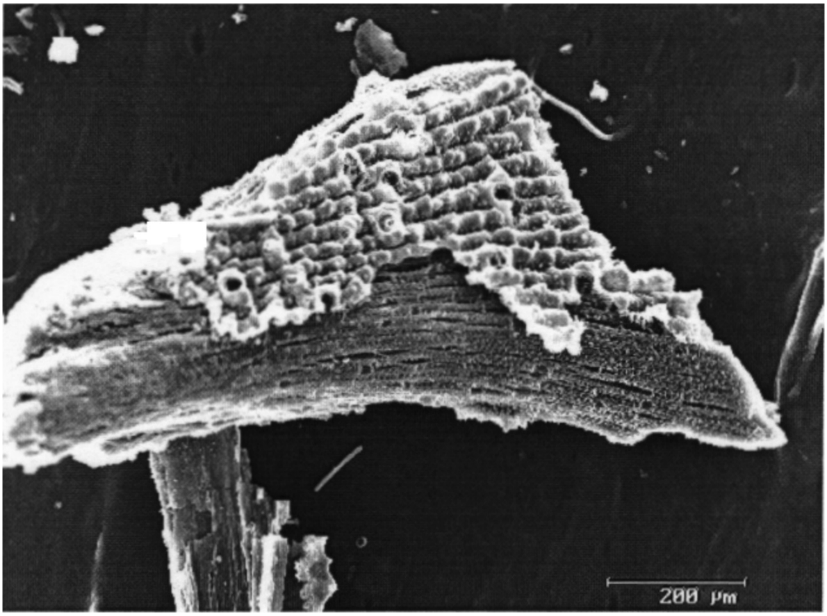

FIGURE 3 SEM photographs of black ash.

response functions such as linear, quadratic, and special cubic functions were tried. The appropriate function was chosen based on the values of lack of fit, R-squared (the multiple correlation coefficient), and PRESS (Predicted Residual Sum of Squares). Adequacy of the response functions was further confirmed by constructing the normal probability plot of the residuals [10]. It has been found that all the properties "η" given in Table 2 can be related through special cubic functions of the type given below:

$$\eta = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3$$

where x_1 = Calcium carbonate, weight fraction; x_2 = white ash, weight fraction; x_3 = black ash, weight fraction.

The coefficients of these equations for the various properties were determined by the previously mentioned software. These equations are the basis on which "trace curves" were constructed.

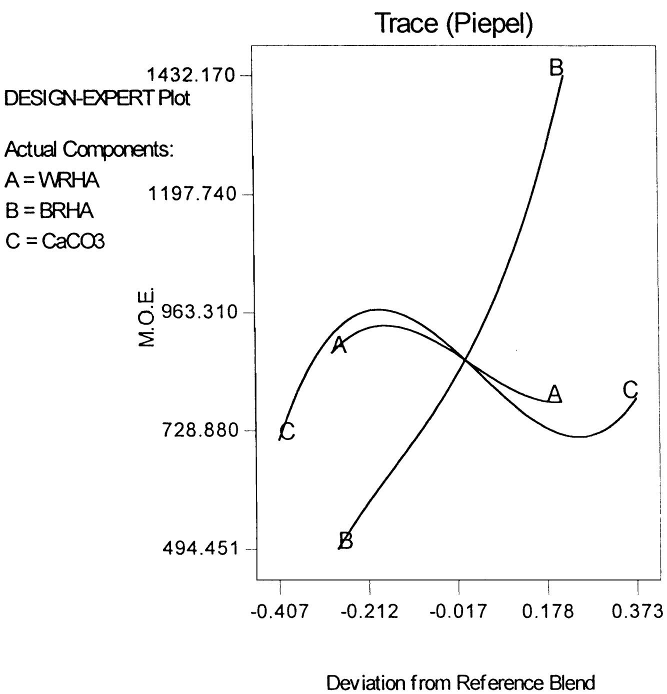

FIGURE 4 Trace plots of the effect of filler composition on the modulus of elasticity.

Effect of Fillers on Modulus of Elasticity (MOE)

The effect of different types of fillers on MOE is shown as trace plots on Figure 4. It can be seen that the MOE increases initially and then decreases on increasing the amount of calcium carbonate. Whereas the white ash decreases the MOE values, black ash increases the same appreciably. The reason for this noteworthy contribution to the stiffness of the moulded material by the black ash can be attributed to the fibrous morphology of the black ash particles as can be seen in the Scanning Electron Microscopic photographs. In fact they are like carbon fiber and this morphology contributes to the stiffness of the moulded product. Thus the increase in MOE with increase of the black ash could be due to the combined effect of the fibrous morphology as well as optimum aspect ratio. Similar results have been reported by Ahmad Fuad et al. [8] when they investigated the effect of black ash as filler in polypropylene-based composites.

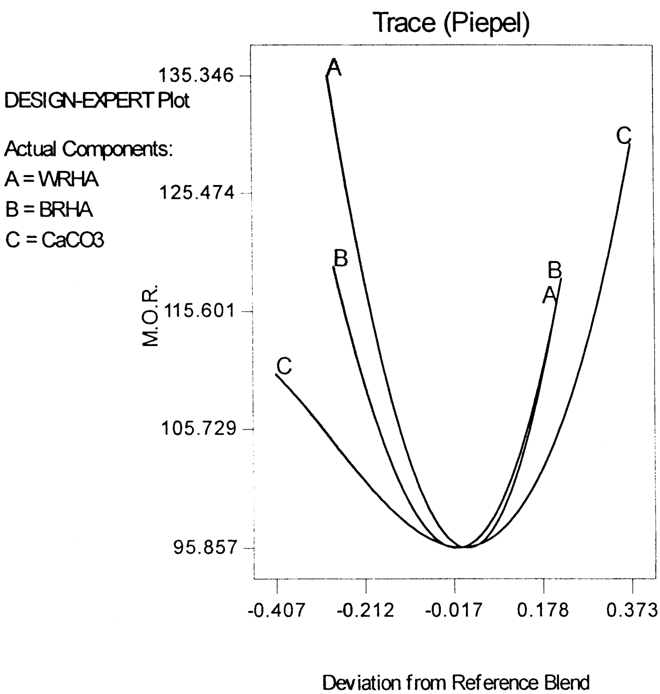

FIGURE 5 Trace plots of the effect of filler composition on the modulus of rupture.

Effect of Fillers on the Modulus of Rupture (MOR)

It can be seen from Figure 5 that as the filler quantities increase, the MOR at first decreases, passes through a minimum, and thereafter increases. At lower filler contents, the resin content is higher and thus the SMC exhibits high flow during compression moulding. Due to the pressure employed in the compression moulding process, excessive flow of the moulding compound results in a loss of matrix material as flash. This results in inadequate matrix content in the mouldings to promote interfiber adhesion. The MOR is thus reduced.

On increasing the filler content further, the flow of the material during the compression moulding decreases and this hard flow is conducive to better compaction and retention of the matrix material without being forced out as flash. Sufficient matrix material is therefore retained in the moulded composite and as a consequence good interfiber bonding is established causing the increase of the MOR.

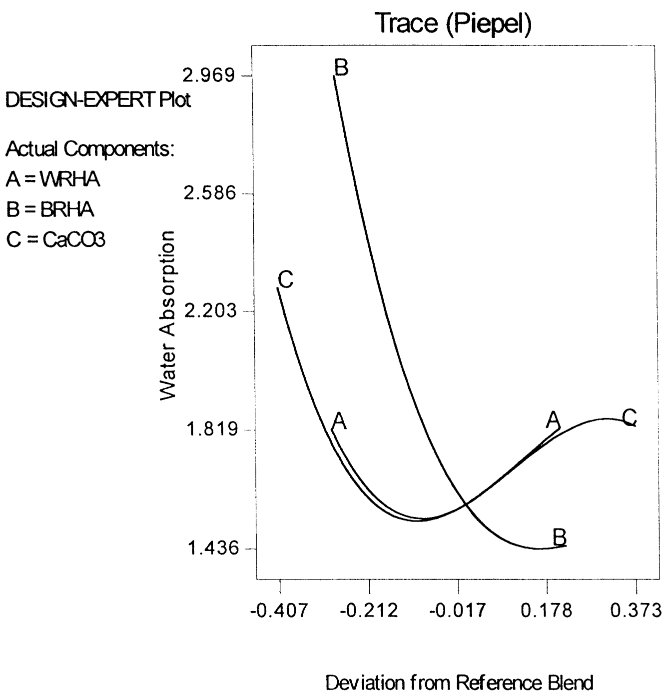

FIGURE 6 Trace plots of the effect of filler composition on the water absorption.

Effect of Fillers on Water Absorption

From Figure 6, it can be seen that the water absorption shows a declining trend with the increase in the quantity of the white ash and black ash. This may be due to the reduction in porosity as the filler content increases up to certain level. The substantial reduction of the water absorption of the composites when the quantity of black ash is increased is quite interesting. It was at first suspected that during the process of production of black ash by incomplete oxidation, some organosilicon compounds could be formed that could function as water repellent. But the ^{29}Si MAS NMR studies furnished no such evidence. The water repellent character of black ash should be due to the hydrophobic nature of carbonaceous residues present on its outer surface. In the case of calcium carbonate filler, the water absorption increases with the increase of the filler content.

Effect of Fillers on Thickness Swelling

Figure 7 shows that white ash does not affect the thickness swelling significantly. Calcium carbonate results in increase in the thickness

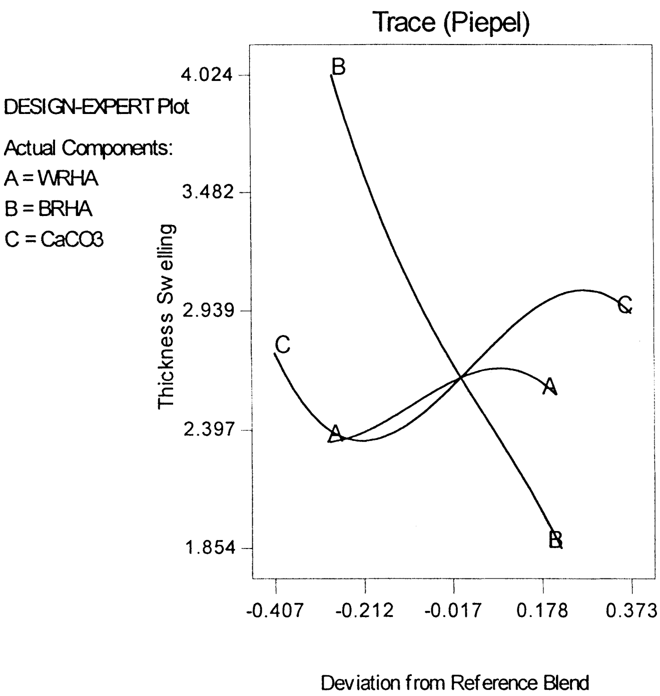

FIGURE 7 Trace plots of the effect of filler composition on the thickness swelling.

swelling after a slight initial reduction. On the other hand increasing the quantity of black ash results in significant reduction in the thickness swelling. The water repellent characteristics of the black ash is therefore evident and this requires more detailed investigation.

REFERENCES

[1] Ahmad Fuad, M. Y., R. Shukor, Mohd. Ishak, Z. A., and Mohr Omar, A. K. (1994). *Plastics, Rubber Composites & Applications*, **24**, 225.

[2] Ahmad Fuad, M. Y., Ismail, Z., Ishak, Z. A. M., and Omar, A. K. M. (1995). *Euro. Poly. J.*, **31**(9), 885.

[3] Beagle, E. C. (1974). *Proc. of Rice-By-Products Utilization International Conf.*, P. I. Valencia, Spain.

[4] Houston, D. F. (1972). *Rice: Chemistry and Technology*, Chap. 12 (Am. Assoc. of Cereal Chem., Minnesota)

[5] Chen, S. S., and Yahoo, A. K. (1992). *J. Perindustr., SIRIM* **2**, 19.

[6] Dalal, A. K., Rao, M. S., and Gokhale, K. V. G. K. (1985). *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 465.

[7] Ahmad Fuad, M. Y., Zaini, M. J., Mohd. Ishak, Z. A., and Omar, A. K. (1994). *J. Elastomer and Plastics*, **26**, 252.

[8] Ahmad Fuad, M. Y., Mustafah, J., and Mansoor, M. S. (1995). *Polymer International*, **38**, 33.

[9] Cornell J. A. (1981). *Experiments with Mixtures* (John Wiley and Sons, New York, NY).

[10] Myers R. H., and Montgomery, D. C. (1995). *Response Surface Methodology: Process and Product Optimization Using Designed Experiments* (John Wiley & Sons., Inc, New York, NY).