5. MATERIALS AND METHODS

The objective of the wider study, of which this work forms part, was to investigate the feasibility of phlogopite-LLDPE composites for building applications. The prime objective was to reduce cost to a minimum. Amongst other factors this also requires minimisation of the expensive binder in the composite. The current study reports on the measurement and prediction of the Young's modulus of such composites. The experimental investigation was conducted in four parts:

- Initial scoping experiments were conducted to determine relevant ranges of the independent variables.
- With knowledge of these preliminary results, a statistical experiment was designed, using the Taguchi approach, to determine the relative contribution of the composition variables.
- Next, a similar approach was followed to evaluate the effect of processing.
- Finally, based on these results a new predictive model for the composite modulus was developed. Additional experiments were also performed in order to verify its validity.

To fully characterise the mechanical properties of composites it is necessary to conduct many different measurements. A composite's tensile properties depend on its micro-structure, interfacial load transfer between two phases, and structural factors such as form, size distribution, aggregation and orientation of the filler. [16] It is important to note that these give complementary information on the material properties. Modulus data, in contrast to impact strength, is not very sensitive to structural defects and the degree of adhesion between the filler and matrix. This is because it is evaluated at low deformations and low strain rates. Tensile strength and elongation-at-break are large scale deformation properties and are more sensitive to structural defects. Filler surface treatment, in general, has a greater effect on the latter properties than on modulus. On the other hand, for the case of laminar composites, flexural tests should also be performed to highlight any interlaminar effects. [26]

5.1 Experimental procedure

Figure 6 outlines the procedure followed to produce the phlogopite-based composite sheets: (Details are provided in Appendix 3)

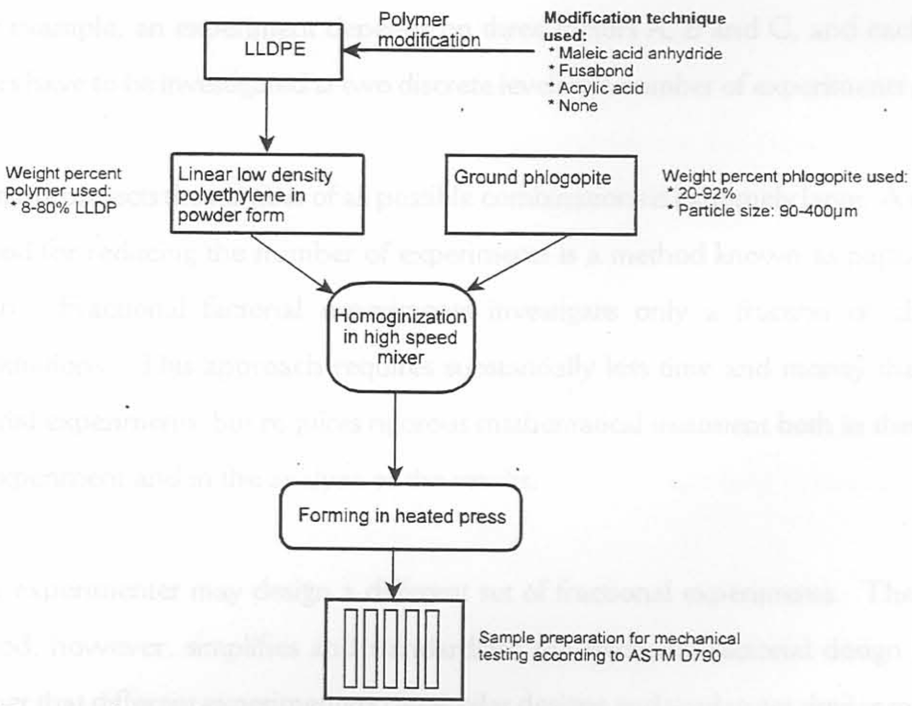

Figure 6: General outline of the experimental procedure followed

Five test pieces were cut from each sheet to obtain the necessary test pieces for a flexural three point bending tests (for bending modulus and yield strength), tensile tests and Izod impact tests. All the tests were performed according to ASTM standards [31,32] at 50% humidity and 25°C.

The Taguchi experimental design technique

The technique used for defining and investigating all possible conditions in an experiment involving multiple factors is known as factorial design. This method enables an experimenter to determine all possible combinations of experimental variables and to identify the best combination for a required result.

If for example, an experiment depends on three factors A, B and C, and each of these factors have to be investigated at two discrete levels the number of experiments are $2^3=8$.

For many projects the number of all possible combinations is extremely large. A customary method for reducing the number of experiments is a method known as partial factorial design. Fractional factorial experiments investigate only a fraction of all possible combinations. This approach requires substantially less time and money than the full factorial experiments, but requires rigorous mathematical treatment both in the design of the experiment and in the analysis of the results.

Each experimenter may design a different set of fractional experiments. The Taguchi method, however, simplifies and standardizes the fractional factorial design in such a manner that different experimenters use similar designs and tend to get similar results. [35]

Taguchi constructed a special set of orthogonal arrays to design his experiment. A typical orthogonal array is shown in Table 4 and Table 5. This array designated by the symbol L_{16} is used to design experiments involving up to four factors at four levels each. Each row represents a trial condition with factor levels indicated by the numbers in the row. The vertical columns correspond to the factors specified in the experiment.

The standardized orthogonal arrays of the Taguchi method facilitates the experimental design process. To design an experiment the most suitable array has to be selected from several pre-defined arrays available, depending on the number of factors and levels used in the particular experiment.

In the Taguchi method the results are analyzed to achieve on or more of the following objectives [35]:

- to establish the best or optimum condition for a product or process
- to estimate the contribution of each individual factor
- to estimate the response under optimum condition

The optimum condition can be identified by studying the main effects of each of the factors. Referring to Table 4, the main effect of e.g weight percentage polymer at level 3 will be the sum of the result of all the trials containing this factor at level 3. The optimum level for this factor will then be the level with the largest (or smallest, if appropriate) main effect. [35]

The analysis of variance (ANOVA) is the statistical treatment most commonly applied to the results of the experiments to determine the percentage contribution of each factor. By studying the ANOVA results for a given experiment it can then be established which are the critical factors, that need control. [35]

5.2 Scoping experiments

Linear low density polyethylene was used as binder. To promote adhesion of the polymer to the surface of the phlogopite, various pre-modified LLDPE were tried, viz. irradiated LLDPE from Gammatron (Pty) Ltd [33], LLDPE compounded with 10% maleic acid anhydride (MAA), LLDPE compounded with 5% MAA and LLDPE compounded with 10% MAA and 1% chain transfer agent (C1) to inhibit cross linking. All the polymers were used in powder form and each formulation was homogenised in a high speed mixer prior to compression moulding. Phlogopite was supplied by FOSKOR Ltd. in South Africa [34] and was milled in a laboratory pin mill to an average particle size of 400μm.

Table 3: Experimental design for the scoping experiments

		Polymer System				
		Pure LLDPE	Irradiated LLDPE	10% MAA 90% LLDPE	5% MAA 95% LLDPE	10% MAA 1% Additive
		Experiment #				
% polymer	5%	1	5	9	13	17
	10%	2	6	10	14	18
	15%	3	7	11	15	19
	20%	4	8	12	16	20

Table 3 shows the experiments performed using the materials mentioned above. Two sheets of each composition were made using compression moulding. The mould had dimensions of 150mm wide by 200mm long. Sheets were produced that were 3.5mm thick. The sheets were hot pressed at 190°C at a pressure of 10 MPa and each sample was left at this pressure for 15 minutes to allow proper heat transfer and complete wetting of the phlogopite by the polymer.

5.3 Composition

Virgin linear low density polyethylene (LLDPE) and various pre-modified forms were used. Modifications included: irradiated LLDPE from Gammatron [33], Fusabond from Du Pont and LLDPE blended with 220 mmol acrylic acid per 100g LLDPE. [21] All the polymers were used in powder form and each formulation was homogenised in a high speed mixer prior to hot pressing.

Phlogopite was pin milled and classified in a dry sieve shaker to the desired particle size range. Table 4 shows the experiments performed using the materials mentioned above, following the L_{16} Taguchi array [35]. The variables particle size, type of polymer modification and mass percentage polymer were investigated at four levels as indicated in Table 4.

Two composite sheets of each composition were prepared using hot press moulding. The mould had dimensions of 150mm wide by 200mm long. Sheets (3.5mm thick) were produced by compression moulding at 190°C at a pressure of 5 MPa for 7 minutes followed by 10 MPa for 13 minutes.

5.4 Processing conditions

Fusabond (ex Du Pont) at 15% by mass was used as binder. Pin milled phlogopite in the size range 180 to 150 μm was used as filler. Table 5 shows the experiments performed using the materials mentioned above, following the L_{16} Taguchi array [35]. Process temperature, pressing time, moulding pressure and the mass per unit area were investigated at four levels as indicated in Table 5.

Two composite sheets of each composition were prepared using hot press moulding. The mould had dimensions of 150mm wide by 200mm long. The testing procedure was similar to that for the composition experiments.

Table 4: Taguchi experimental array showing the individual experiments with the results obtained.

Level	Polymer type	wt% polymer	particle size
1	PE	8	90
2	γ-PE	14	125
3	Fusa	20	180
4	AA	24	250

PE - Pure LLDPE
γ - Irradiated LLDPE
Fusa - Fusabond
AA - LLDPE blended with 220 mmol acrylic acid per 100g LLDPE

Exp#	Column			Results (MPa)			
	1	2	3	Flexural modulus	Flexural Stress at Yield	Young's modulus	Tensile strength
1	1	1	1	195	3.9	170	0.3
2	1	2	2	1341	9.5	1641	2.3
3	1	3	3	2333	12.6	2001	2.6
4	1	4	4	1725	16.3	924	1.9
5*	2	1	2	0	0	0	0
6	2	2	1	657	6.1	990	0.8
7	2	3	4	1453	10.8	1045	2.6
8	2	4	3	1185	10.9	1311	1.9
9	3	1	3	289	4.9	1619	0.3
10	3	2	4	1892	12.7	1178	1.6
11	3	3	1	1575	14.4	1042	1.8
12	3	4	2	1276	13	1115	2.6
13	4	1	4	140	3.7	1379	0.6
14	4	2	3	1303	7.2	1112	2.6
15	4	3	2	1481	11.3	1084	1.9
16	4	4	1	1334	11.4	900	2.1

* The composite produced in this experiment was too weak for mechanical testing and therefore no results are available for this particular trial.

Table 5: Taguchi experimental array showing the individual experiments with the results obtained.

Level	Temp °C	Time min	Press MPa	*kg/m^2
1	150	5	5	5
2	200	10	6.5	6.7
3	250	15	8	8.3
4	300	20	10	10

Exp#	Column				Results (MPa)			
	1	2	3	4	Flexural modulus	Flexural Stress at Yield	Young's modulus	Tensile strength
1	1	1	1	1	1215	12.2	1880	1.8
2	1	2	2	2	1348	13.8	1856	2.1
3	1	3	3	3	1549	15.3	1724	2.1
4	1	4	4	4	3003	19.1	1439	2.7
5	2	1	2	3	1745	15.8	1186	1.9
6	2	2	1	4	1394	15.2	1729	2.5
7	2	3	4	1	2609	22.6	1564	4.0
8	2	4	3	2	2025	17.1	2374	2.8
9	3	1	3	4	2010	16.9	2044	3.8
10	3	2	4	3	2254	18.5	2110	1.5
11	3	3	1	2	904	11.2	1393	2.1
12	3	4	2	1	2269	23.4	1377	4.4
13	4	1	4	2	2327	23.9	1634	2.2
14	4	2	3	1	1909	21.7	1850	4.5
15	4	3	2	4	2424	21.3	1766	1.1
16	4	4	1	3	1525	17.1	2260	2.1

* The mass of material used per m^2 determined the thickness of the sheet.

5.5 Modelling

Table 6 shows the experiments performed:

Table 6: Experiments for model verification

Method†	mass% polymer	Particle size range*
Compression moulding	8-30% in 2% increments	• 125-180 μm • 250-300 μm
Injection moulding	50, 60 and 80%	• 125-180 μm • 250-300 μm

† Based on the planar isotropic nature of the material the Young's modulus of the composite would only slightly be influenced by the method

* Although the particles were sieved, image analysis revealed that the average aspect ratio was constant at about 18

Young's modulus

All samples were prepared and tested in the same manner as described before.

Voidage

The voidage of all the samples was calculated after measuring the density of the samples, using Equation 7.

$$\phi = 1 - \frac{\rho_{composite}}{\rho_{theoretical}} \tag{7}$$

The theoretical density can be calculated from the individual phases' densities, based on the mass fraction of each:

$$\frac{1}{\rho_{theoretical}} = \frac{x_p}{\rho_p} + \frac{x_m}{\rho_m} \tag{8}$$