6. RESULTS

The results obtained in the various experimental sections will be discussed separately as outlined in chapter 5.

6.1 Initial scoping experiments

The results of the mechanical property measurements are presented in Figures 7 to 9. Note that the samples that contained 5% LLDPE were too weak for mechanical testing.

6.1.1 Bending modulus

With the exception of the 5% MAA sample, Figure 7 shows that modification of the LLDPE improves the bending modulus. This may be attributed to improved interfacial adhesion and to a lesser extent to an increase in modulus of the matrix.

It is well known that maleic anhydride modified LLDPE provides excellent adhesion to polar surfaces. The significant improvement in bending modulus of 5% and 10% MAA compared to virgin LLDPE probably reflects an interfacial adhesion effect. In contrast the improvement when the irradiated LLDPE is used, probably reflects matrix stiffening due to cross-linking. It is also known that the use of MAA grafted polyethylene also leads to cross-linking. Therefore the 10% MAA data reflects a combination of adhesion improvement and matrix cross-linking. This is confirmed by the 10% MAA plus 1% C1 data set in which cross-linking was largely prevented.

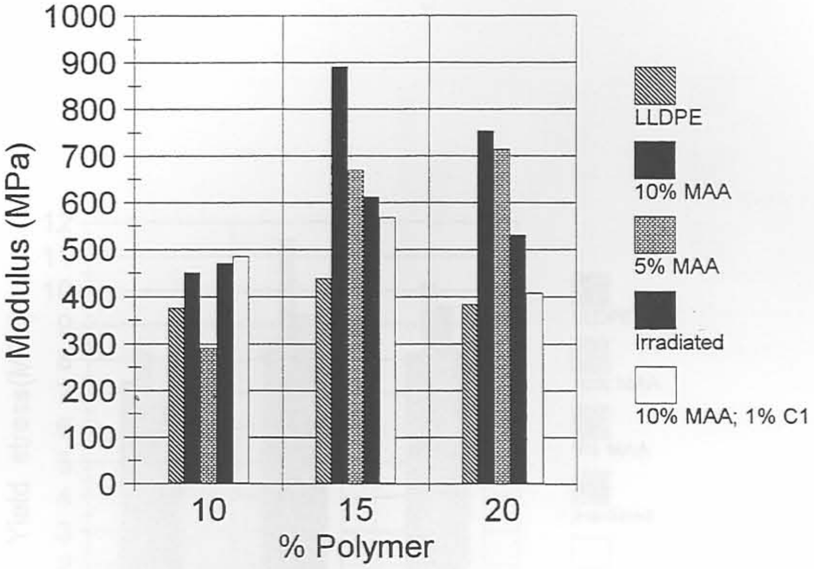

Figure 7: Bending modulus for various modified LLDPE / Phlogopite composites

It is interesting that in all cases the modulus reached a maximum value at about 15% polymer content. This is an unexpected result. It can be rationalised as follows: firstly phlogopite has a much higher modulus than the polymer. At very low concentrations of polymer the phlogopite flakes are not effectively bound and this lowers the effective modulus. At high polymer levels the lower modulus of the polymer becomes significant, again lowering the modulus of the composite.

6.1.2 Yield strength

Figure 8 shows the effect of polymer content and type on the yield stress of the composites. Once again optimum yield stress is obtained at 15% polymer loading. Since it is a large-deformation property, yield stress is expected to be more sensitive to the degree of adhesion between the polymer and the phlogopite than the degree of cross-linking of the matrix. This is confirmed by the fact that there is very little difference in yield stress of the virgin LLDPE and irradiated (cross-linked) samples. Further confirmation for this conclusion is provided for the small differences observed between the cross-linked and uncross-linked 10% MAA samples. Best performance was achieved using the 10% MAA LLDPE as matrix material.

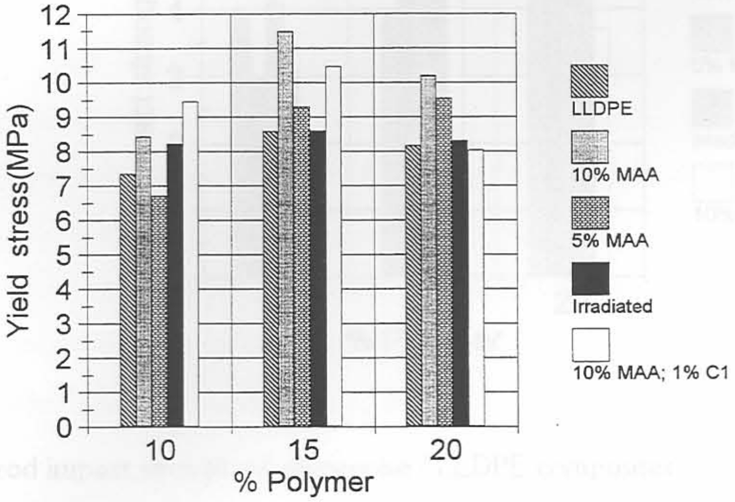

Figure 8 Stress-at-yield for various modified LLDPE / phlogopite composites

6.1.3 Izod Impact strength

Figure 9 shows the impact strength of the various composites tested. From these results it can be seen that the impact strength increases with increasing polymer content, as it is expected. The various modifications to the LLDPE do not influence the impact strength significantly.

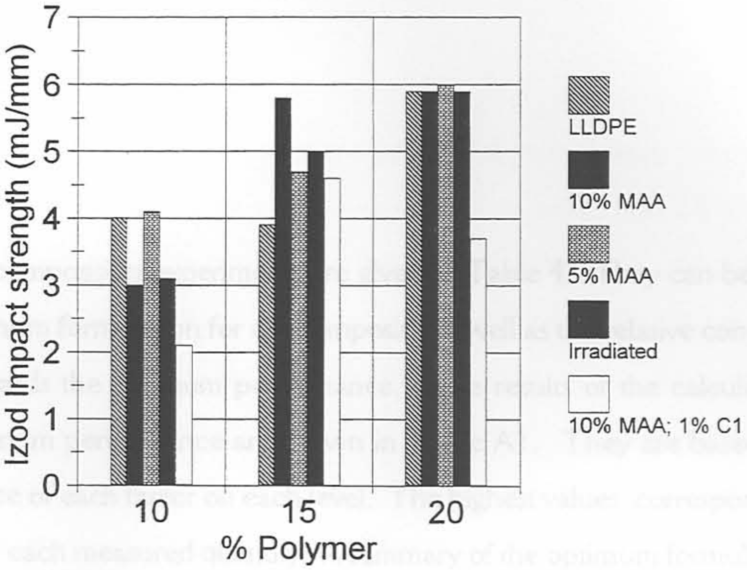

Figure 9: Izod impact strength of phlogopite / LLDPE composites

6.1.4 Appearance

The sheets that were made had an appearance similar to wood composites that are used as dry walling in the building industry. The advantageous properties imparted by the phlogopite, such as low thermal conductivity, good sound proofing and fire resistance will make it ideal for this application.

6.1.5 Conclusions

The initial experiments showed that the bending modulus and yield strength reached optimum values at 15% polymer whereas impact strength increased with polymer content. With respect to the polymer modifications used, it appears that interfacial adhesion is a more important factor than cross-linking. It is assumed that the stiffness of the polymer is increased by the degree of cross- linking. Optimal results were obtained using the 10%

MAA grafted LLDPE. It is assumed that this modification provided improved adhesion and improved matrix stiffness.

6.2 Composition

The results of the composition experiments are given in Table 4. They can be used to determine the optimum formulation for the composite as well as the relative contribution of each factor towards the optimum performance. The results of the calculations to determine the optimum performance are shown in Table A1. They are based on the average performance of each factor on each level. The highest values correspond to the best formulation for each measured quantity. A summary of the optimum formulation for each measured quantity is shown in Table 7.

As shown by Kovačevic et al. [16] and Wakeman et al. [26], tensile measurements provide a better indication of interfacial adhesion than flexural measurements. The present results for tensile stress at break, for the composites bonded with acrylic acid modified LLDPE provided confirmation for this observation.

Table 7: Optimum formulation for each of the mechanical properties

	Polymer type	% Polymer	particle size
Flexural modulus	LLDPE	20%	180-250μm
Flexural stress at yield	Fusabond	24%	180-250μm
Young's modulus	Fusabond	20%	125-180μm
Tensile strength at break	AA	20%	125-180μm

For filled polymeric systems, smaller particles usually have the best reinforcing effect. It is evident from the data, however, that in the case of these composites, larger particles are preferred. It was previously mentioned that more polymer is needed to wet smaller particles. Since the amount of polymer in the system is to be kept as low as possible larger particles are preferred. Analysis of variance revealed that particle size only contributed significantly in terms of the Young's modulus of the composite. For the other measured variables, the effect of particle size was overshadowed by the large effect of the amount of polymer used.

The results (Table 4) also indicate that more polymer is not always better for the composite properties. Only in the case of flexural stress at yield, was 24% polymer preferred over 20% polymer. The reason for this is most likely due to the role of the interface. At low polymer content there is not enough polymer to wet the phlogopite and effectively bind the composite. At higher polymer concentration, more polymer is present at the interface and the phlogopite may start acting as a weakness in a polymer matrix, which is generally true for polymer systems where the filler is added at quantities more than 60%. From the results of the Taguchi experiments one can see that 20% polymer will generally be the optimum.

6.2.1 Flexural properties

Figure 10 shows the ANOVA results for flexural modulus and flexural stress at yield. A 10% level of significance was used to determine the significance of each factor.

It is interesting to note that for the flexural modulus, particle size does not contribute significantly. When this factor is pooled with the error term it becomes even more clear that the amount of binder is the most important factor relating to the properties of the composite.

It was previously shown [16,26] that the effect of adhesion is more important for ultimate properties than for modulus data. The ANOVA results show that the use of Fusabond improves the yield strength. This effect was not apparent from the modulus data, which suggested virgin LLDPE as the optimum polymer for flexural modulus. In the case of yield strength, the amount of polymer is once again the most important parameter influencing the properties of the composite.

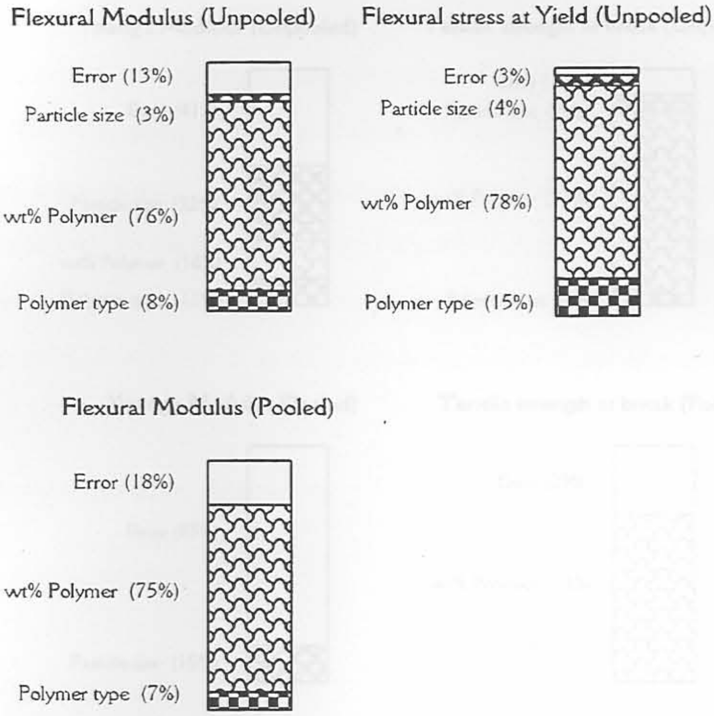

Figure 10: Relative contribution of the composition variables towards the flexural properties (pooled and unpooled)

6.2.2 Tensile properties

Figure 11 shows the ANOVA results for the tensile properties of the composite at a 10% level of significance. It is evident from Figure 11 and Table A2 that none of the measured variables played a significant role in determining the Young's modulus of the composite. This is attributed to the large intrinsic variability in mechanical properties of this complicated system. The low contribution of polymer content factor, to explain the observed variance, can also be attributed to non-linear effects. Furthermore, the Young's modulus is known not to be sensitive to the effects of particle size and efficiency of adhesion. The amount of binder, therefore, also becomes less important in this case, because the stiffening effect of the phlogopite on the polymer is evident even at very low concentrations.

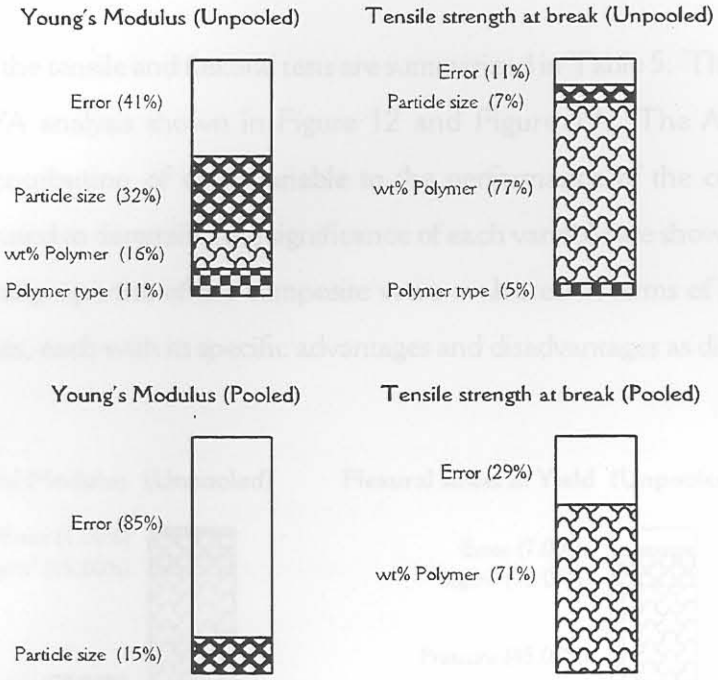

Figure 11: Relative contribution of the composition variables towards the tensile properties (pooled and unpooled)

The tensile strength of the composite is also influenced the most by the amount of polymer used. For a high tensile strength the adhesion between the polymer and the phlogopite needs to be very good. For good adhesion more polymer is needed to wet the surface properly. In other words, using too little polymer, regardless of the particle size, the polymer will not effectively wet the surface thus limiting stress transfer between the polymer and the phlogopite.

6.3 Processing parameters

The data from the tensile and flexural tests are summarized in Table 5. These were used for the ANOVA analysis shown in Figure 12 and Figure 13. The ANOVA results indicate the contribution of each variable to the performance of the composite. The variance ratios used to determine the significance of each variable are shown in Table A4. The mechanical properties of the composite were evaluated in terms of its flexural and tensile properties, each with its specific advantages and disadvantages as discussed earlier.

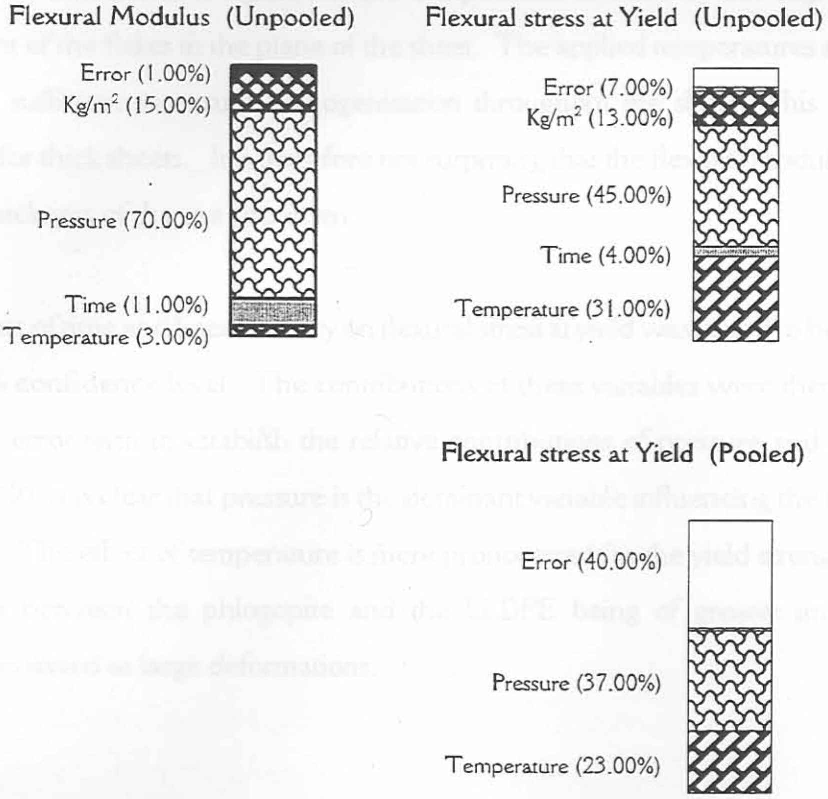

Figure 12: Relative contribution of processing variables towards flexural properties (pooled and unpooled)

6.3.1 Flexural properties

Figure 12 shows the ANOVA results for flexural modulus and flexural stress at yield. A 10% level of significance was used.

It is clear from Figure 12 and Table A4 that all the variables contributed significantly to the flexural modulus. Of the variables investigated, moulding pressure dominated while moulding time and temperature had the smallest effect.

The flexural modulus, or rigidity, of the composite is affected by the degree of parallel alignment of the flakes in the plane of the sheet. The applied temperatures and pressures must be sufficient to ensure homogenisation throughout the sheet. This is difficult to achieve for thick sheets. It is therefore not surprising that the flexural modulus is affected by the thickness of the test specimen.

The effect of time and linear density on flexural stress at yield was found to be insignificant at a 90% confidence level. The contributions of these variables were therefore pooled with the error term to establish the relative contributions of pressure and temperature. (Figure 12) It is clear that pressure is the dominant variable influencing the flexural stress at yield. The effect of temperature is more pronounced for the yield strength in view of adhesion between the phlogopite and the LLDPE being of greater importance for properties tested at large deformations.

6.3.2 Tensile properties

Figure 13 shows the ANOVA results for the tensile properties of the composite.

Tensile tests have more value where the adhesion of the binder to matrix material is of importance. Figure 13 and Table A4 show that none of the variables investigated played a significant role in determining the Young's modulus. Although pressure was the dominant variable it was still insignificant even if all the other variables are pooled with the error term. This implies that the moulding temperatures and times investigated were sufficient to ensure the attainment of ultimate properties for the composite.

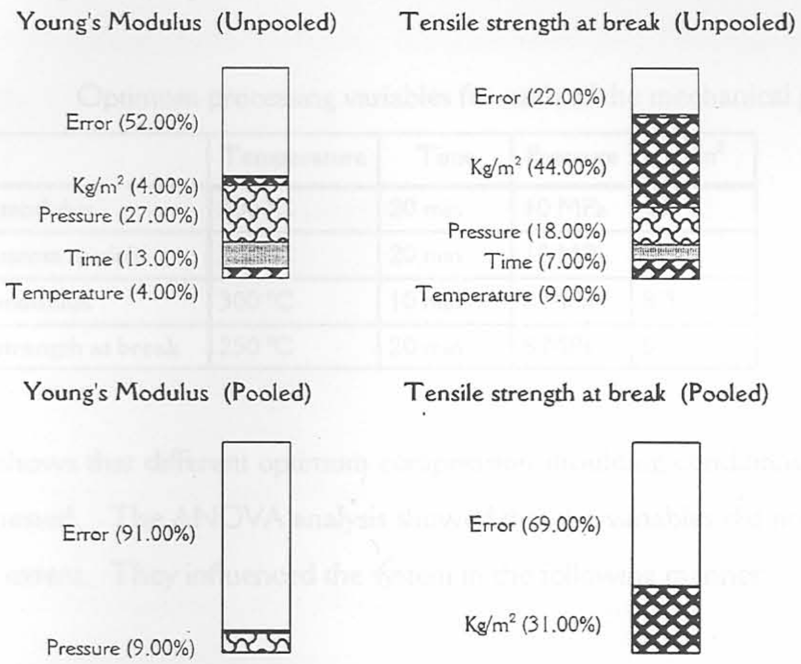

Figure 13: Relative contribution of processing variables towards the tensile properties (pooled and unpooled)

The tensile stress-at-break is a good indication of the adhesion properties of the composite. Figure 13 shows that only the mass of material used per unit area influenced this property.

For the present processing conditions, the optimum amount of material for tensile stress at yield was at the minimum value tested, 5 kg/m^2 material per sheet. (Table 8) Only the flexural modulus and tensile strength of the composite are dependant on the thickness of the composite (mass per area used) as the material has a laminar structure and is therefore inhomogeneous. The flexural modulus of the material is increased when more phlogopite flakes align in plane of the composite; more plates in plane of the composite is the result of a higher amount of material per unit area. The tensile strength of the composite is decreased by an increase in thickness of the composite. This is probably due to inhomogeneity in the thicker composites owing to pressure transmission and heat transfer effects. Visual inspection of the thick samples showed poor bonding at the centre. This may imply that heat transfer from the heated press to the material was the limiting factor. Proper melting and compaction of the material was not achieved for the thick samples.

Table 8: Optimum processing variables for each of the mechanical properties

	Temperature	Time	Pressure	kg/m^2
Flexural modulus	300 °C	20 min	10 MPa	10
Flexural stress at yield	300 °C	20 min	10 MPa	5
Young's modulus	300 °C	10 min	8 MPa	8.3
Tensile strength at break	250 °C	20 min	8 MPa	5

Table 8 shows that different optimum compression moulding conditions exist for each property tested. The ANOVA analysis showed that the variables did not contribute to the same extent. They influenced the system in the following manner:

- **Temperature.** Higher temperatures will reduce the viscosity of the polymer binder improving its fluidity. This aids wet-out and compaction.
- **Time.** Enough time should be allowed for sufficient heat transfer to take place to ensure complete melting of the binder.
- **Pressure.** Sufficient pressure must be applied to ensure efficient compaction. Pressure aligns the particles such that their greatest area is exposed perpendicular to the applied pressure. Misalignment will result in the formation of voidage which will cause a reduction in mechanical properties
- **Mass per unit area.** The mass of material used in the mould will ultimately determine the thickness of the composite. The thickness of the sheet will influence the heat transfer from the mould to the inner parts of the composite.