

## **CHAPTER 8 RESULTS AND DISCUSSION**

The results obtained from the various experiments carried out are discussed in this chapter. To begin with, the process results are discussed. The main aim was to establish the effect of the composition (polymer and wax content) on the mechanical, thermal, flow, expansion and surface texture properties of the urea moulding compounds. Two-way ANOVA was used as a statistical tool to analyse the experimental results. The Charpy impact test results are used to explain how the two-way ANOVA procedure was applied in this study. The results obtained on the properties are then compared against the industrial benchmark, i.e. the “cooked” urea-based moulding compound. This is shown in Appendix E.

### **8.1 Process results**

#### ***8.1.1 Oven***

After heat treatment for 8 hr in an oven at 80°C, the PVOH powdered granules had absorbed all of the glycerol plasticiser. The glycerol had diffused into the PVOH. The processing temperature was sufficiently low to allow direct compounding with urea.

#### ***8.1.2 Single-screw extruder***

Trials were initially done using a single-screw extruder. It was difficult to extrude EVA compounds but it proved impossible to compound the PVOH system. This is attributed to the high melt viscosity of the latter. A single-screw extruder is not a suitable mixer for the urea/PVOH/wax blend because it mixes by means of a shear mechanism without an elongational flow component. Shear mixing is inefficient when there is a large difference in the melt viscosities of the components.

### ***8.1.3 Two-roll mill***

It was possible to compound the urea/PVOH/wax blend using a two-roll mill. This is because this type of compounding allows extensive mixing to take place due to the elongational flow that occurs at the entrance of the nip.

### ***8.1.4 Intermeshing co-rotating twin-screw extruder***

EVA urea-based moulding compounds were successfully compounded using a co-rotating twin-screw extruder. The twin-screw compounder was a suitable mixer as the kneader blocks provide for elongational mixing. However, it proved difficult to pull the weak EVA strands directly into the pelletising unit.

### ***8.1.5 Injection-moulding***

The pelletised urea/PVOH/wax blend was injection-moulded into tensile test specimens without mould-release problems. However, at a high glycerol content the parts started to stick to the mould's surface.

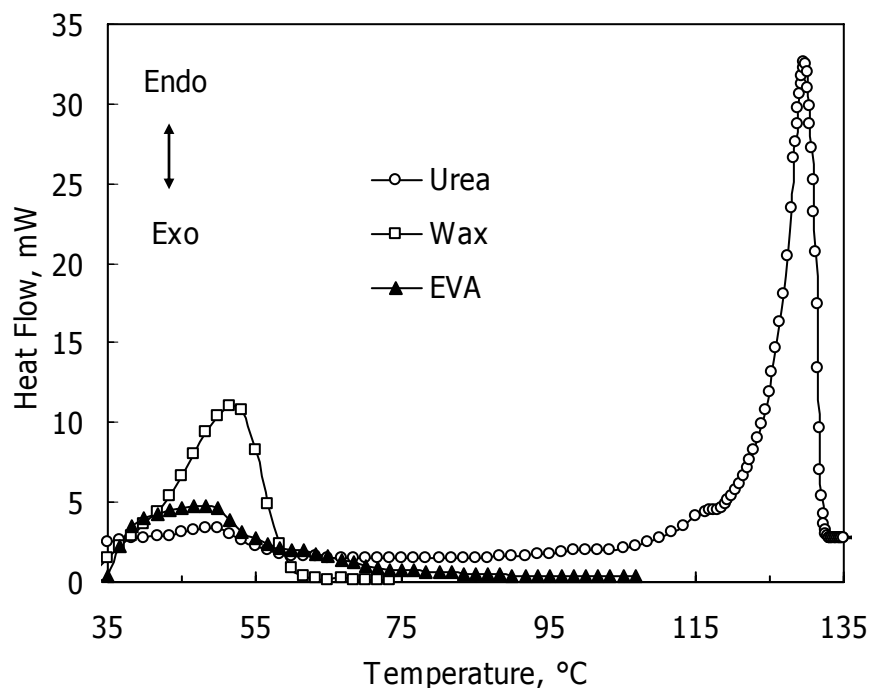
In the case of EVA-based moulding compounds, it was difficult to injection-mould blends containing 80% or more of urea. This could be because the urea content has reached its critical filler level, where there is not enough EVA and liquid wax to fill the voids between the urea particles. However, injection-moulding was easily achieved at a urea content of 70% with all EVA and wax combinations.

## **8.2 Thermal properties**

### ***8.2.1 Differential scanning calorimetry***

Differential scanning calorimetry (DSC) can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe the glass transition

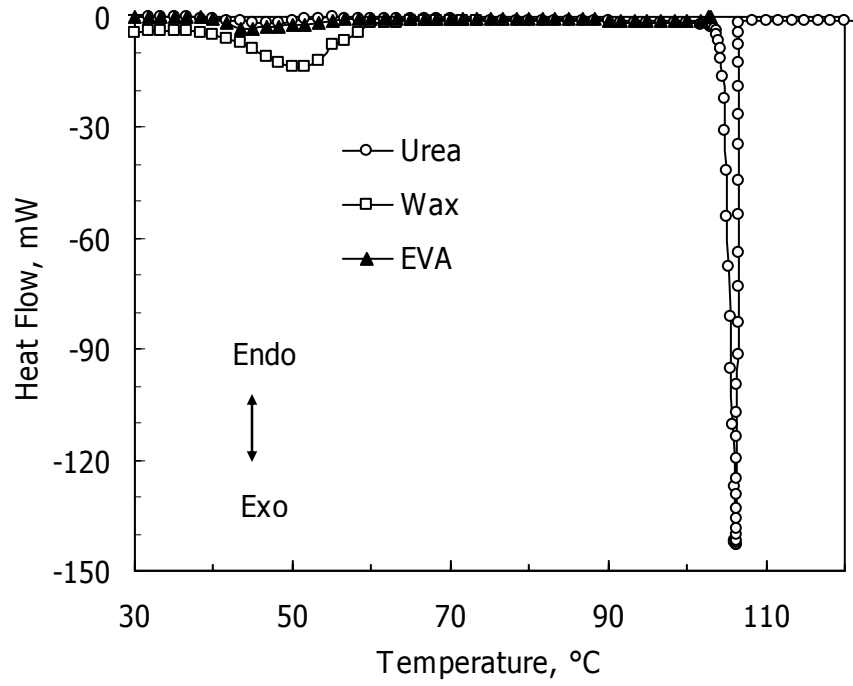
temperature ( $T_g$ ) and the melting temperature, and also fusion and crystallisation events. In this section DSC was applied to study the thermal behaviour of urea-based moulding compounds during heating and cooling. This can aid the understanding of the processing conditions needed to process the urea moulding compounds.



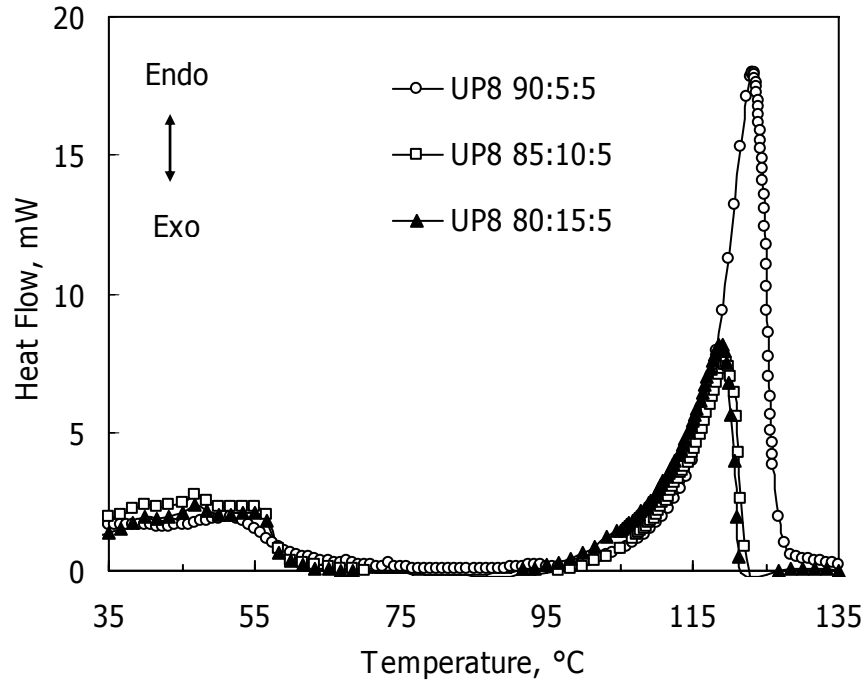
**Figure 28: DSC heating curve of pure samples**

Figure 28 shows the DSC heating run for the pure components. It reveals melting ranges of 50-55°C and 55-61°C for the wax and EVA respectively. The melting peak of urea is centered at ca. 132°C. In the cooling run shown in Figure 29, urea shows a sharp crystallisation peak at 108°C. The wax and EVA show broader crystallisation exotherms at 55 and 57°C respectively.

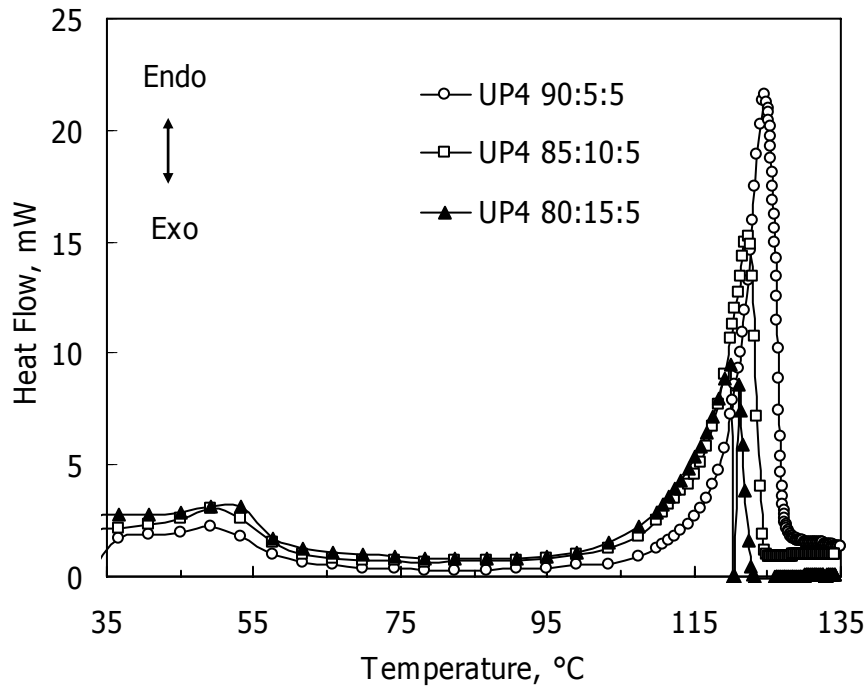
The DSC curves for PVOH plasticised with glycerol were featureless in the temperature range 25–140°C. This suggests that the compound had an amorphous structure.



**Figure 29: DSC cooling curve of pure samples**

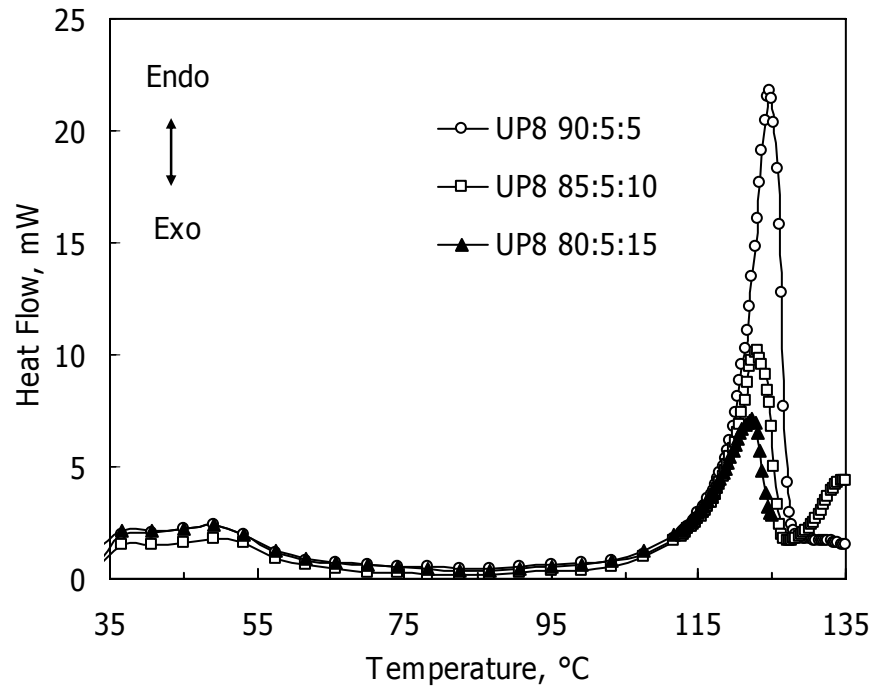


(a)

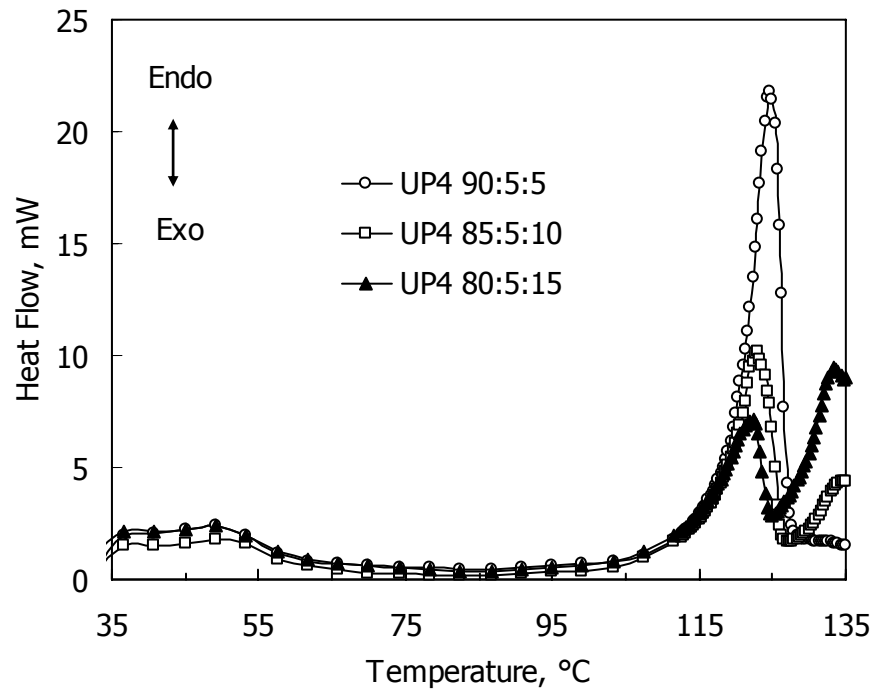


(b)

**Figure 30: Effect of increasing the polymer content on the DSC heating curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and 40 phr**



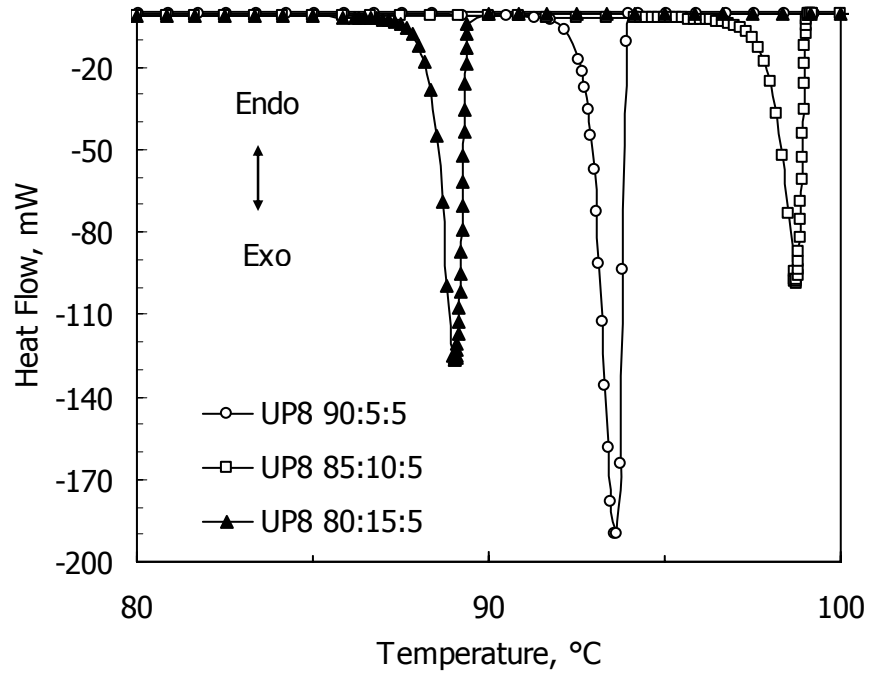
(a)



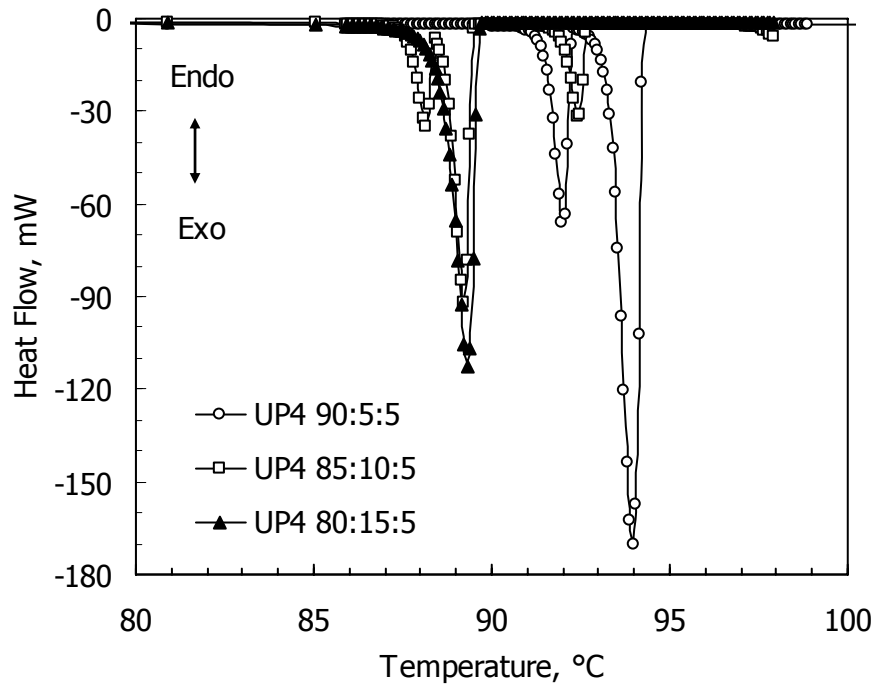
(b)

**Figure 31: Effect of increasing the wax content on the DSC heating curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr**

The effects of increasing the polymer and wax content on the thermal properties of PVOH moulding compounds are shown in Figures 30 and 31 and Table 12. At any degree of plasticisation, up to three endothermic peaks are observed in the heating curve and three exothermic peaks in the cooling curve. The endothermic peak centered at ca. 50°C is assumed to be the melting of the wax. The large endothermic peak at ca. 120°C is due to melting of the urea. The high-temperature endothermic peak, above the melting point of urea, is only observed at wax contents of 10% and 15%. It is not present when the wax content is 5%. Furthermore, the intensity of this peak increases with wax content. Therefore it is considered to be due to interaction of wax with urea, i.e. the formation of a wax-urea inclusion compound. The exothermic peaks observed in the cooling curve correspond to the crystallisation of these phases.



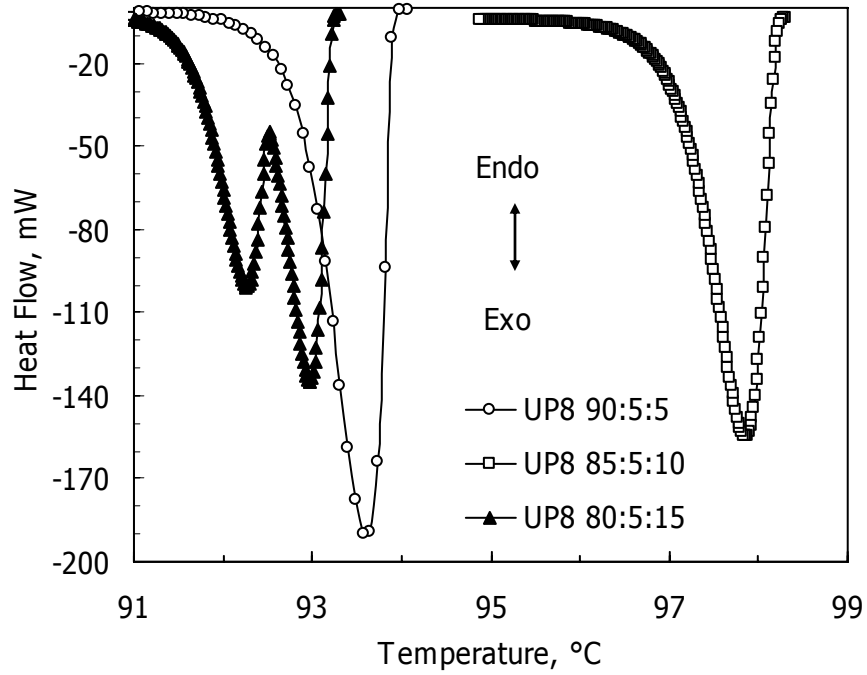
(a)



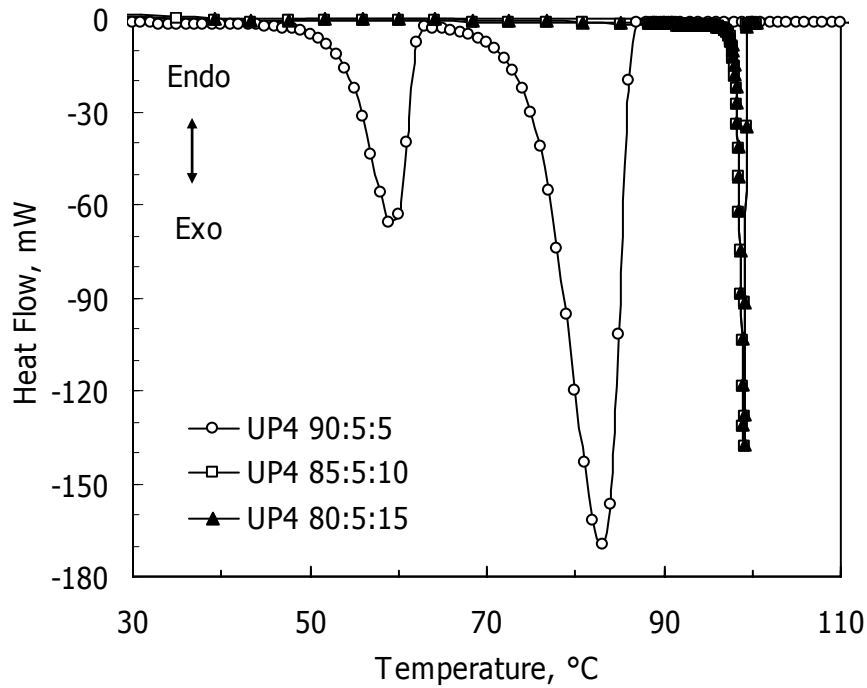
(b)

**Figure 32: Effect of increasing the polymer content on the DSC cooling curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr**





(a)



(b)

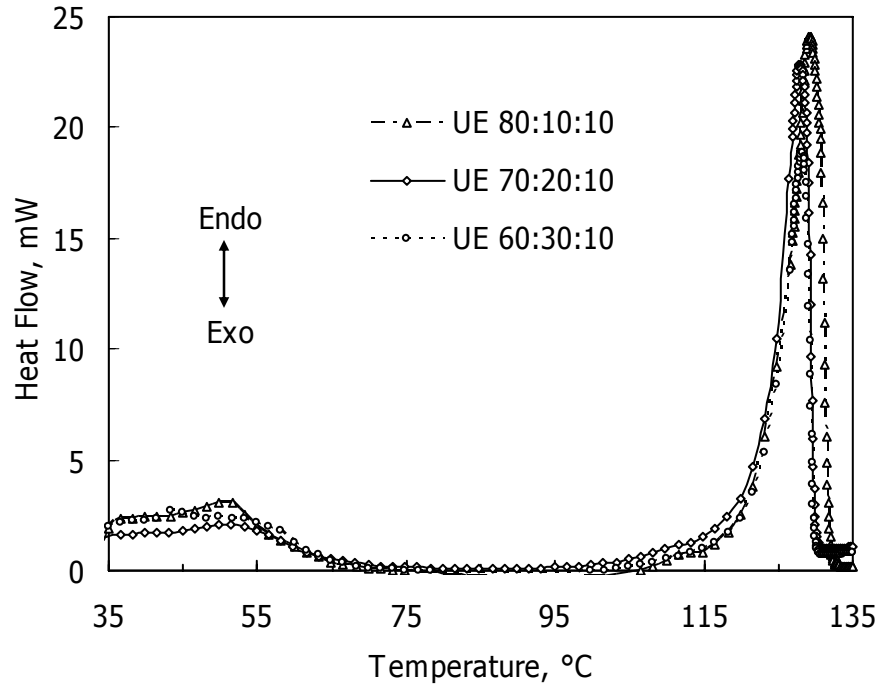
**Figure 33: Effect of increasing the wax content on the DSC cooling curves of PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr**

The location of the cooling exothermic peak provides an indication of the ease of crystallisation of the compound. If large under-cooling is required before the compound crystallises, it implies that crystallisation is lethargic and that it will take a long time. Fast cycle times in injection moulding imply that rapid crystallisation is desired. Figure 32 (UP8 90:5:5 – UP8 80:15:5) shows the effect of PVOH content at a constant wax level of 5%. Note that the crystallisation occurs fastest at the intermediate PVOH content of 10%. The composition with 15% PVOH required the largest under-cooling before crystallisation commenced. Similar behaviour was shown by the UP4 compounds with the added complication that multiple crystallisation exotherms were found. The reason for this complex behaviour and non-linear composition-dependence is not understood at present. An explanation is beyond the scope of this technical investigation. Figure 33 (UP8 90:5:5 – UP8 80: 5: 15) shows the effect of wax content at a constant PVOH level of 5%. Here too crystallisation was fastest at the intermediate wax content of 10%. The composition with 15% wax showed multiple crystallisation exotherms. This could be due to the crystallisation of urea and a wax-urea clathrate. Non-homogeneity of the material owing to poor mixing or phase separation provides another possible explanation for the multiple crystallisation peaks.

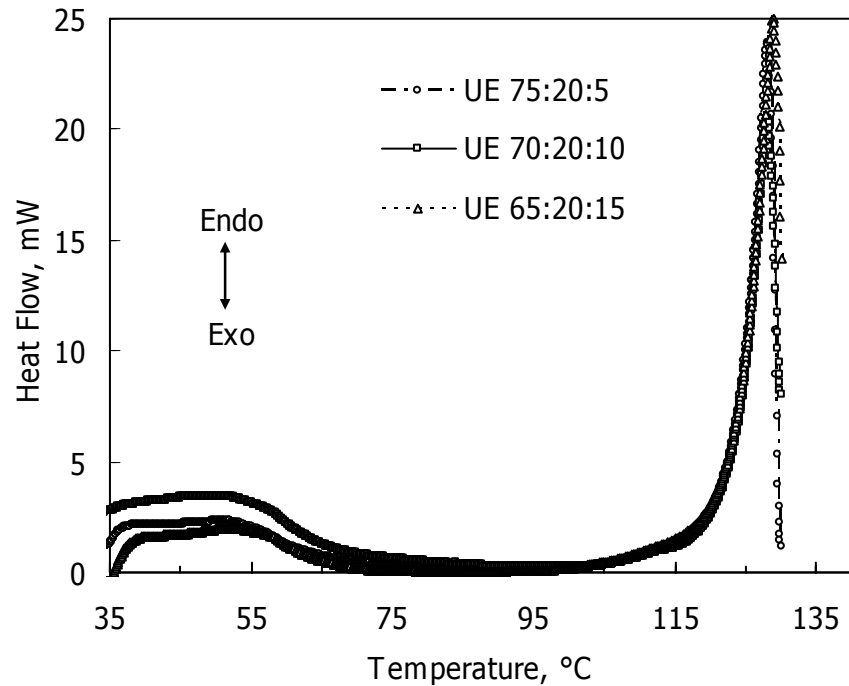
**Table 12: Parameters obtained from DSC measurements for investment casting patterns on the large-peak and pure samples**

Sample	$T_{o,m}$	$T_m(^{\circ}C)$	$\Delta H_m$ (kJ/kg <sup>-1</sup> )	$T_c(^{\circ}C)$	$T_{p,c}(^{\circ}C)$
Urea	125,9	130,2	147,2	108,1	106,2
Wax	43,4	53,4	105,1	56,2	53,3
UP8 90:5:5	116,3	120,1	103,3	96,2	93,6
UP8 85:10:5	111,3	120,7	79,6	100,3	98,7
UP8 80:15:5	112,3	119,1	68,9	89,3	88,9
UP8 80:5:10	114,1	121,1	51,1	97,2	96,5
UP8 80:5:15	121,5	122,3	35,3	92,3	88,6
UP4 90:5:5	122,5	125,3	102,6	93,1	89,6
UP4 80:10:5	118,1	121,1	89,3	87,2	88,7
UP4 80:15:5	116,2	120,9	72,5	82,1	81,6
UP4 80:5:10	117,3	120,9	52,8	96,6	94,1
UP4 80:5:15	118,2	123,1	39,1	96,8	94,9

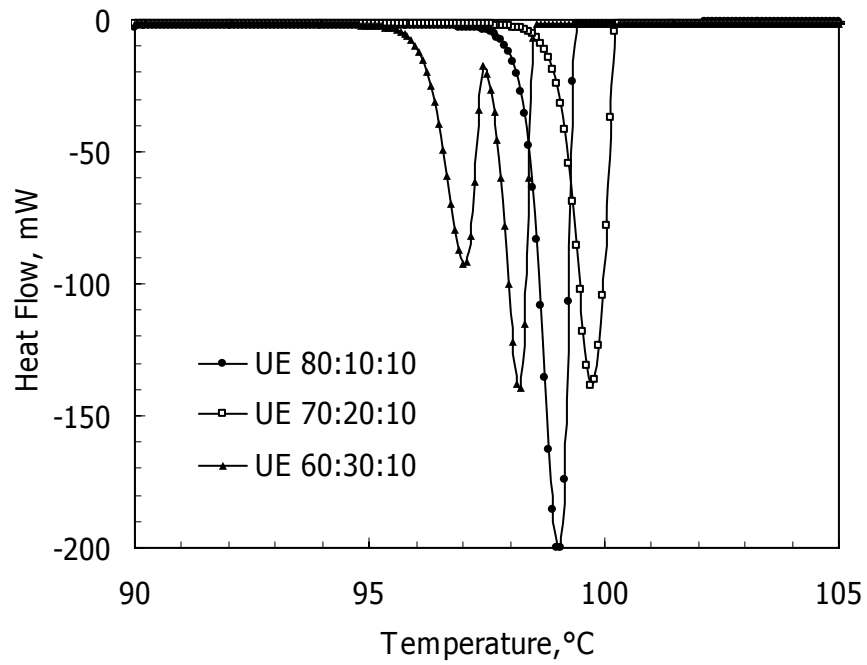
Table 12 shows that, as expected, the enthalpy of melting decreases with an decrease in the urea content. This is not only because the content is reduced, but also because higher melting complexes of urea are also formed



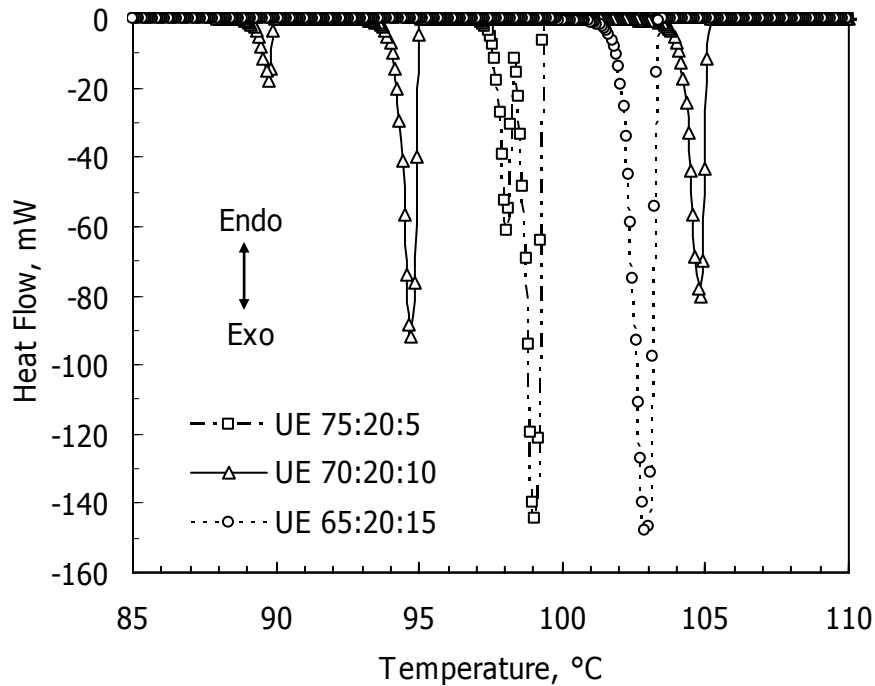
**Figure 34: Effect of increasing the polymer content on the DSC heating curves of the EVA moulding compounds**



**Figure 35: Effect of increasing the wax content on the DSC heating curves of the EVA moulding compounds**



**Figure 36: Effect of increasing the polymer content on the DSC cooling curves of the EVA moulding compounds**



**Figure 37: Effect of increasing the wax content on the DSC cooling curves of the EVA moulding compounds**

**Table 13: Properties obtained from differential thermal analysis of urea peak and EVA/wax blends**

Sample	$T_{o,m}$ EVA/Wax Blend	$\Delta H_m$ (kJ/kg <sup>-1</sup> ) EVA/Wax blend	$T_{o,m}$ Urea	Urea $\Delta H_m$ (kJ/kg <sup>-1</sup> )
EVA	59,3	15,2	-	-
UE 80:10:10	58,9	20,0	136,3	144
UE 70:20:5	59,0	24,4	135,2	131
UE 70:20:10	60,8	28,5	135,0	125
UE 65:20:15	62,9	30,9	135,9	133
UE 60:30:10	59,8	31,6	135,0	115

The effects of increasing the EVA and wax content on the thermal properties of EVA moulding compounds are shown in Figures 34 to 37 and Table 13. The results show two endothermic peaks and multiple exothermic peaks respectively. The small lower melting peak at ca. 60°C corresponds to the EVA and wax present in the blend. The EVA resin melts at 60-62°C and freezes at 62°C. The EVA freezes at the same temperature as paraffin wax. These two components co-crystallise, which allows the EVA resin to reinforce the wax. In the melt the wax acts as an internal lubricant as it interacts and dissolves in the polymer (EVA).

The large melting endotherm at ca. 133°C is due to urea. The melting of the urea occurs at higher temperatures than in the PVOH compounds. This could be due to the poor compatibility of the EVA and wax with urea: the low melt solubility leads to lesser melting point depression. This could explain why an increase in wax or EVA content does not affect the melting peak position as shown in Figures 34 and 35.

The effects of increasing the polymer and wax content on the cooling curve exotherm are shown in Figures 36 and 37. There is no consistent trend to explain the effect of the wax or polymer. Multiple exothermic peaks are more pronounced at high wax content (15%) at a constant polymer content of 20%. This could be due to the formation of inclusion compounds with different crystallisation behaviours. The possibility also exists that the material is inhomogeneous due to poor mixing.

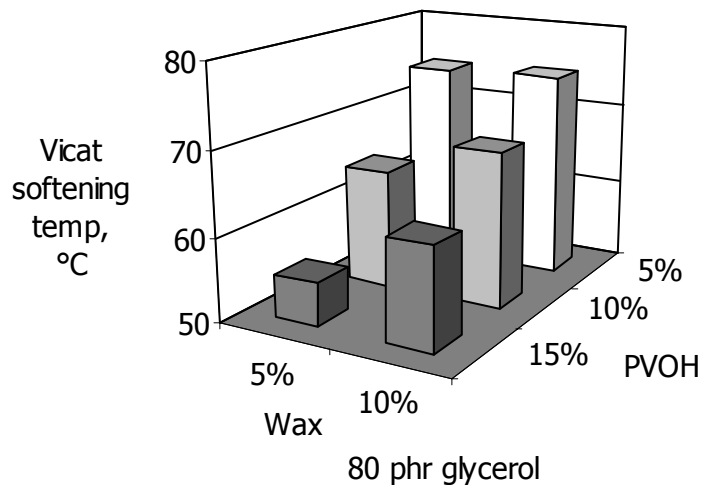
As shown in Table 13, an increase in either the wax or EVA content increases the heat of melting and the EVA/wax peak increases. The increment is less significant in the case of EVA and could be explained by its amorphous nature. The peak of the heat of melting of urea decreases with an increase of either wax or EVA.

The melting and multiple crystallisation temperatures of PVOH moulding compounds are slightly lower compared with EVA moulding compound. The industrial cooked urea-based compound presented the lowest melting temperature at ca. 107°C this is shown in Appendix E. This could be explained by the fact that PVOH reacts with molten urea, forming urethane compounds with lower melting points.

### ***8.2.2 Vicat softening temperature***

Vicat softening is a comparative technique that provides an indication of the relative softness of a material. It is a standardised test method described by ASTM 1525 and ISO 306. It is determined as the temperature at which, under a specified load (in the present study), a flat-ended needle enters to a depth of 1 mm.

In this study the Vicat softening temperature of the urea-based compounds was compared with that of the cooked urea formulation. Materials with a higher Vicat softening point are expected to offer enhanced property retention at elevated temperatures. This has obvious implications for storing, handling and transporting conditions.



**Figure 38: Softening temperature of the PVOH (80 phr glycerol) moulding compounds**

Figure 38 shows that the softening temperature increases with an increase in the wax and a decrease in the polymer content. The current PVOH compounds had higher softening temperatures than the cooked urea moulding compound (benchmark) which shows are hardness.

### 8.3 Mechanical properties

#### 8.3.1 Charpy impact test

Impact testing is a mechanical procedure used to check the ability of a material or an object to withstand a high loading rate. This is quantified as the energy or the force required to fracture the sample.

#### Experimental data analysis design (two-way ANOVA Charpy impact test)

There is always anxiety about the analysis of data generated from an experiment. It is important to take time and effort to arrange the experiment correctly to guarantee that the data

obtained is adequate to respond to questions of concern as clearly and efficiently as possible. In this study factorial experimental designs were used. In such designs the effects of more than one factor on a given response variable are considered. Factorial experimental designs allow the effect of a factor on the response variable to be determined and also whether separate factors may have a mutual effect.

To this end a linear model is postulated and analysis of variance (ANOVA) is used to test for the significance of the factors. Two-way ANOVA is a way of studying the effects of two factors separately, e.g. the direct effects of the wax and polymer contents, and of the wax and polymers together (the interaction effect). The advantage of factorial designs over single factorial experiments is that they are more efficient and they allow interactions to be detected. The two-way ANOVA approach is illustrated here using the experimental data obtained from the Charpy impact test and the three-point bending test (flexural strain, flexural stress, modulus of elasticity, work done) for the EVA and PVOH urea-based moulding compounds. A systematic example of how the two-way ANOVA was carried out is shown in the case of Charpy impact test. The same technique is applied for the three-point bending experimental data results.

The pattern moulding compound has two defining composition characteristics, namely the wax and polymer additive levels. It is reasonable to ask whether a performance property, e.g. the Charpy impact strength, varies with the polymer and wax contents. Thus these levels can be regarded as two predictors that may explain differences in measured Charpy impact strengths. There could be an overall difference in Charpy impact strength due to a difference in the polymer content. There is possibly a difference in the Charpy impact strength due to differences in wax content (irrespective of the polymer). These effects are called "additive".

Two-way ANOVA was used to find out whether the physical property data of the moulding compound is affected by the presence of the wax and polymer additives. In effect, two-way ANOVA checks whether data from two groups have a common mean. One-way ANOVA and two-way ANOVA differ in that the groups in two-way ANOVA have two categories that may define several performance characteristics instead of one.



Finally, there could be synergy or antagonism in a physical property due to interactions between the additives. Such interaction effects are impossible to detect unless there are duplicate observations for at least some combinations of the additives. Two-way ANOVA is a special case of the linear model and its form is defined as follows:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \quad (30)$$

The subscripts in this model have the following meaning: with row index  $i$ , column index  $j$ , and repetition index  $k$ . Here  $y_{ijk}$  is a matrix of observations, e.g. Charpy impact strength. The quantity  $\mu$  denotes the overall mean Charpy impact strength.  $\alpha_i$  is a matrix whose columns are the deviations of each compound's Charpy impact strength (from the mean Charpy impact strength) which are attributable to the wax concentration used. All values in a given column of  $\alpha_i$  are identical, and the values in each row of  $\alpha_i$  sum to 0.  $\beta_j$  is a matrix whose rows are the deviations of Charpy impact strength (from the mean Charpy impact strength) which are attributable to the polymer concentration used. All values in a given row of  $\beta_j$  are identical, and the values in each column of  $\beta_j$  sum to 0.  $\gamma_{ij}$  is a matrix of interactions. The values in each row of  $\gamma_{ij}$  sum to 0, and the values in each column of  $\gamma_{ij}$  sum to 0.  $\varepsilon_{ijk}$  is a matrix of random errors or "disturbances". F statistics are used to do hypothesis tests to find out whether a physical property value is the same across all additive 1 levels, additive 2 levels and additive1-additive 2 pairs (after adjusting for the "additive" effects).

The impact strength data was subjected to ANOVA using the Matlab script files ImpactUP8, ImpactUP4 and ImpactEVA for the PVOH- and EVA-based moulding compounds respectively. This is shown in Appendix G. The natural logarithm of the Charpy values was chosen as the response variable. The output obtained from running this script file is shown in Tables 14 to 16 below. It presents a two-way ANOVA for Charpy impact strength data. Matlab's function ANOVA2 returns the p-values from these tests. These values assume that the random disturbances  $\varepsilon_{ijk}$  in the model equation are independent and normally distributed with constant variance. The linear regression model equations are also used to fit the model; these are shown in equations 31 to 33 below. The experimental data and the predicted data are then compared to establish a fit as shown in Figures 39 to 41 below.

**Table 14: Two-way ANOVA for Charpy impact strength for the urea-PVOH-wax compound containing 80 phr glycerol**

<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	6,86	2	3,43	62,53	< 0,0001
PVOH	20,38	2	10,19	185,64	< 0,0001
Wax * PVOH	0,18	4	0,0457	0,83	0,5135
Error	1,98	36	0,0549		
<i>Total</i>	<i>29,40</i>	<i>44</i>			

F is the F statistic

**Table 15: Two-way ANOVA for Charpy impact strength for the urea-PVOH-wax compound containing 40 phr glycerol**

<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	0,385	2	0,1924	5,39	0,0090
PVOH	6,244	2	3,1219	87,44	< 0,0001
Wax * PVOH	0,615	4	0,1537	4,3	0,0060
Error	1,285	36	0,0357		
<i>Total</i>	<i>8,529</i>	<i>44</i>			

**Table 16: Two-way ANOVA for Charpy impact strength for the urea-EVA-wax compounds**

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	4,866	2	2,4330	44,77	< 0,0001
PVOH	21,221	5	5,3052	97,62	< 0,0001
Wax * EVA	0,032	4	0,0107	0,2	0,8981
Error	2,174	40	0,0544		
<i>Total</i>	<i>28,293</i>	<i>49</i>			

Linear regression was performed using the Matlab regress function and the script files ImpactUP8Linear, ImpactUP4Linear and ImpactEVALinear for the PVOH- and EVA-based moulding compounds respectively. This is shown in Appendix G. Linear regression yielded the following equations:

PVOH (80 phr glycerol):

$$Y_{Charpy} = \exp(-0,2604 - 9,540 X_{wax} + 16,339 X_{PVOH}) \quad (r^2 = 0,9133) \quad (31)$$

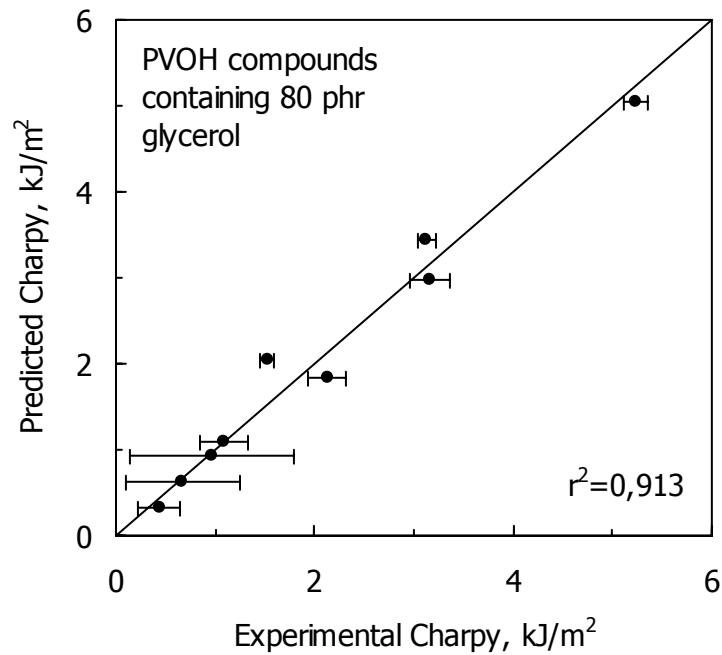
PVOH (40 phr glycerol):

$$Y_{Charpy} = \exp(-0,4416 - 5,272 X_{wax} + 5,491 X_{PVOH} + 36,32 X_{wax}X_{PVOH}) \quad (r^2 = 0,715) \quad (32)$$

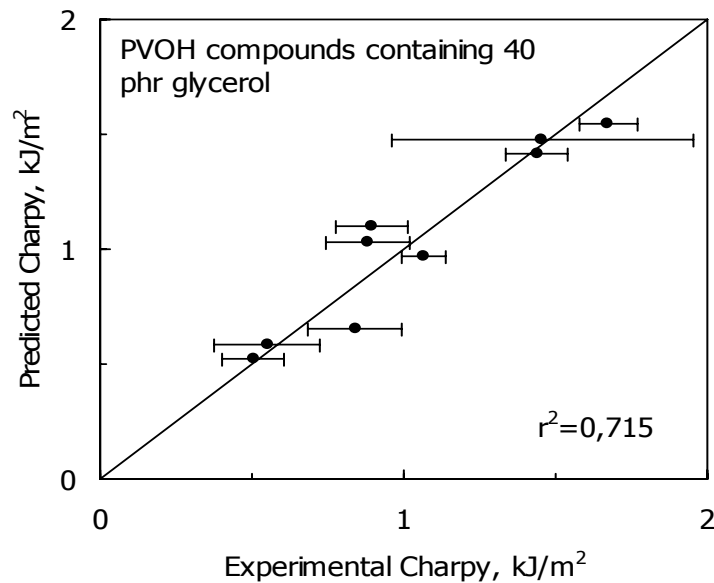
Urea-EVA-wax:

$$Y_{Charpy} = \exp(-2,059 + 2,411 X_{wax} + 11,50 X_{EVA}) \quad (r^2 = 0,991) \quad (33)$$

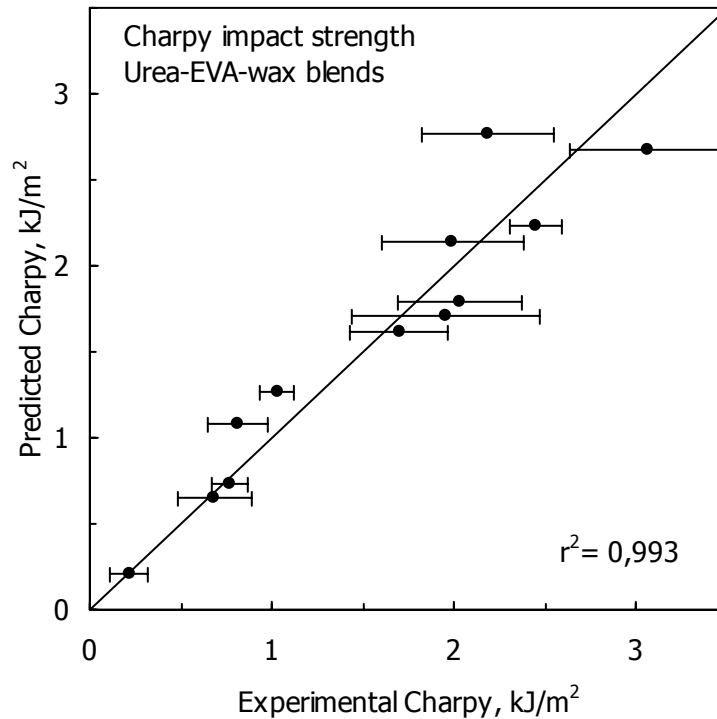
The predictions are compared against the experimental data in Figures 38 to 40.



**Figure 39: Comparison between predicted and experimental Charpy impact strength for quadratic model fit of the urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 40: Comparison between predicted and experimental Charpy impact strength for quadratic model fit of the urea-wax-PVOH (40 phr glycerol) compounds**

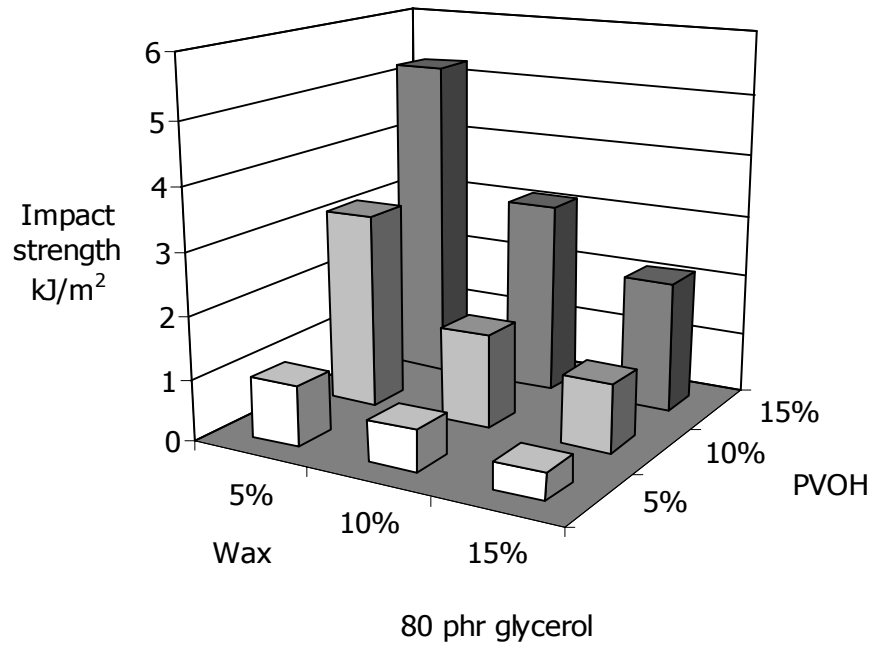


**Figure 41: Comparison between predicted and experimental Charpy impact strength for linear model fit of the urea-EVA-wax compounds**

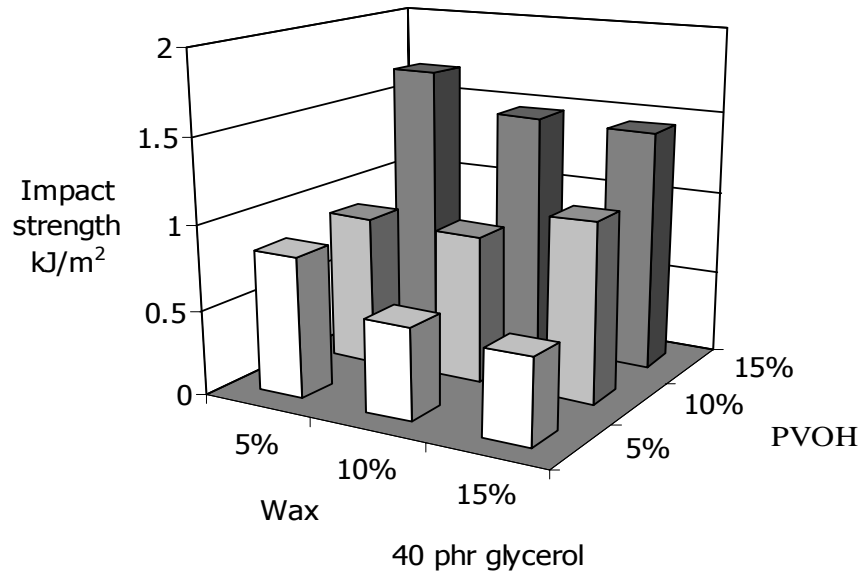
### Data analysis

The two-way ANOVA results for the PVOH urea-based moulding compounds containing 80 phr and 40 phr glycerol, and for the EVA moulding compounds are shown in Tables 14 to 16.

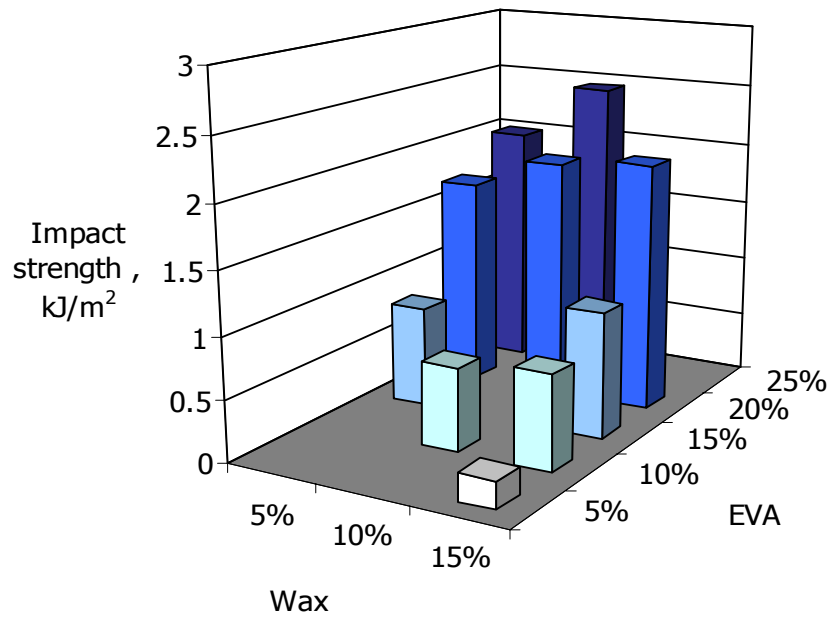
It is concluded that the polymer and wax contents and their interaction are significant in all three cases. The experimental average impact test results are shown in Figures 42 to 44. In the case of the EVA and urea-wax-PVOH (80 phr glycerol) moulding compounds, the model fits, with over 91% of the total variation in the data about the average explained. A poor fit, with only 78% of the total variation in the data about the average explained, was shown by the urea-wax-PVOH (40 phr) moulding compound. The average results of the data analysed are depicted in Figures 41 to 43 below.



**Figure 42: Charpy impact strength of the urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 43: Charpy impact strength of the urea-wax-PVOH (40 phr glycerol) compounds**



**Figure 44: Charpy impact strength of the urea-EVA-wax compounds**

The results given in Figures 42 and 43 shows that the impact strength increases as the PVOH content is increased, as is expected at any degree of plasticisation. An increase in the wax content affects the break results to a very small extent at any degree of plasticisation. This is because PVOH is highly hydrophilic, wax is hydrophobic and there seems to be no interaction between them.

An increase in the degree of plasticisation from 40 to 80 (per hundred resin) phr improves the impact strength. This is attributed to the lowering of the glass transition temperature ( $T_g$ ) of the PVOH binder as the amount of plasticiser is increased. The net effect is an increase in the flexibility and elongation to break of the binder.

As expected, Figure 44 shows that the impact strength increases with EVA content. Adding wax provides a marginal improvement. This is attributed to the compatibility of the wax-EVA blend. The Charpy impact strength data show that the PVOH-urea moulding compound is seven times tougher than the EVA-urea compound. This difference could be due to urea-polymer interactions: urea has the ability to form strong hydrogen bonds with the hydroxyl groups of PVOH. In the case of the EVA moulding compounds, the acetate group is expected to interact more weakly with the urea. A second factor is the difference in molecular masses: the PVOH had a much higher molecular mass than the EVA. It is well known that polymer properties improve with molecular mass. Lastly, the PVOH moulding compounds have a superior impact strength compared with the industrial cooked urea moulding compound. This is because part of the urea might have degraded at the high processing temperatures used in the cooking process.

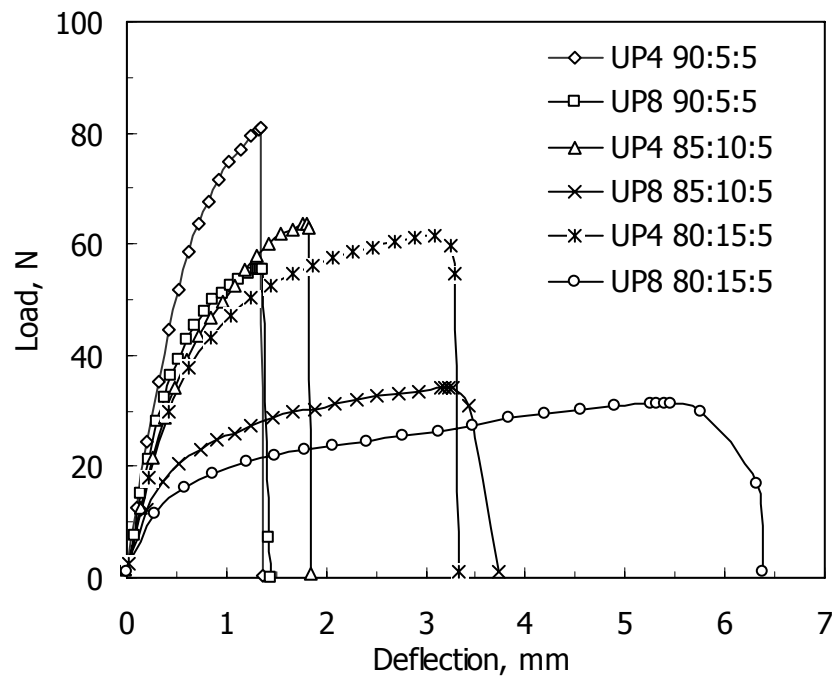
### ***8.3.2 Three-point bending test***

The three-point bending test measures the flexural stress-strain response of the material. From such curves one can determine values for the modulus of elasticity in bending, the flexural stress and the flexural strain. The main advantage of a three-point flexural test is that it can be used to characterise very brittle material such as that being studied here. Additional advantages include the ease of the specimen preparation and testing. Sample of ceramics cannot be “gripped” in the same way as normal strength test. This is another use for 3 point bend test.

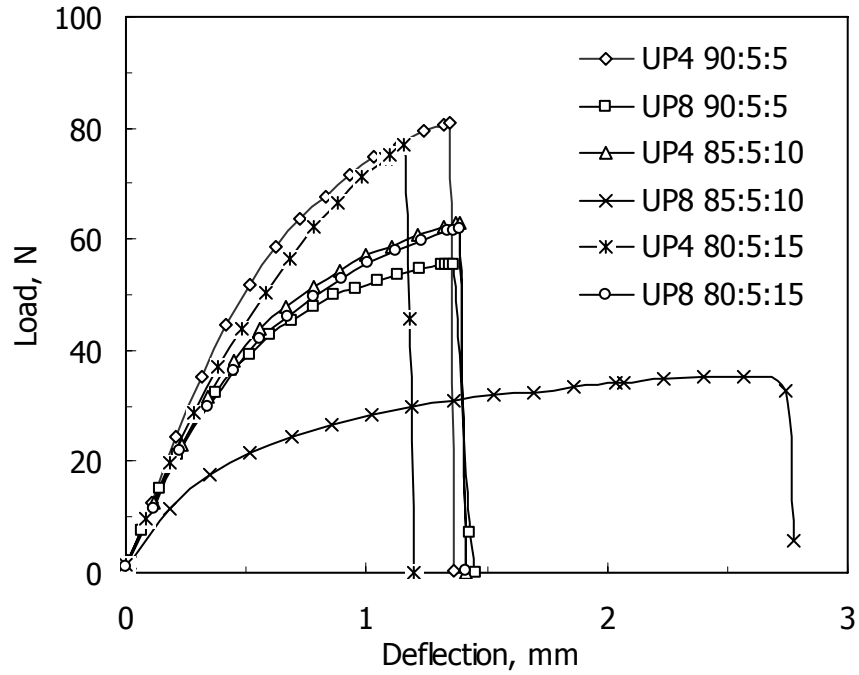


### Load deflection curves

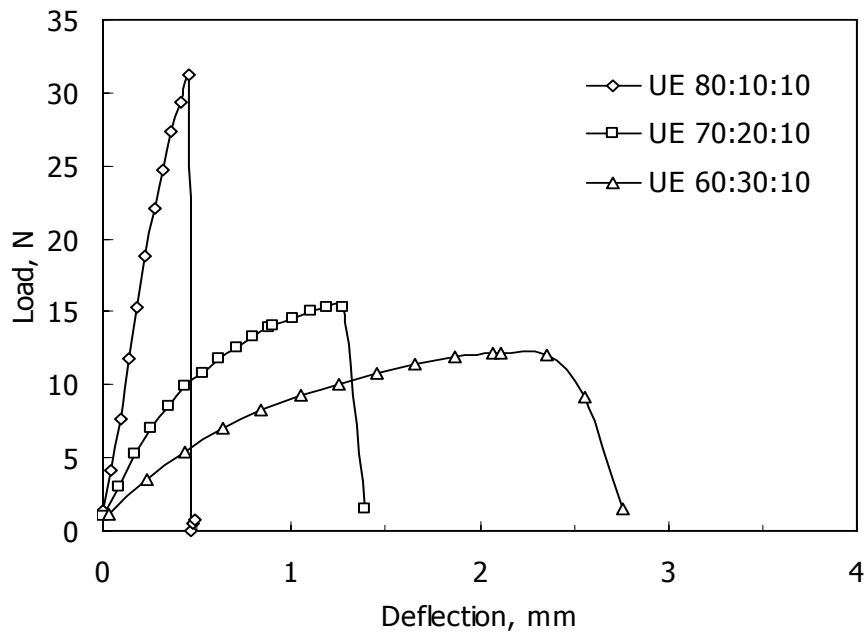
The load deflection curves are the raw data obtained from the flexural test that gives an indication of the toughness and strength of the moulding compound. Using load and deflection values, the flexural strain and stress are calculated from the standard equations described in equation 7 and 8 in the literature study using ASTM D70. The load deflection curves are also used to calculate the modulus of elasticity. This is done by calculating the steepest slope under load deflection curve and using equation 9 in the literature. Fracture energy is calculated as the area under the load deflection curve.



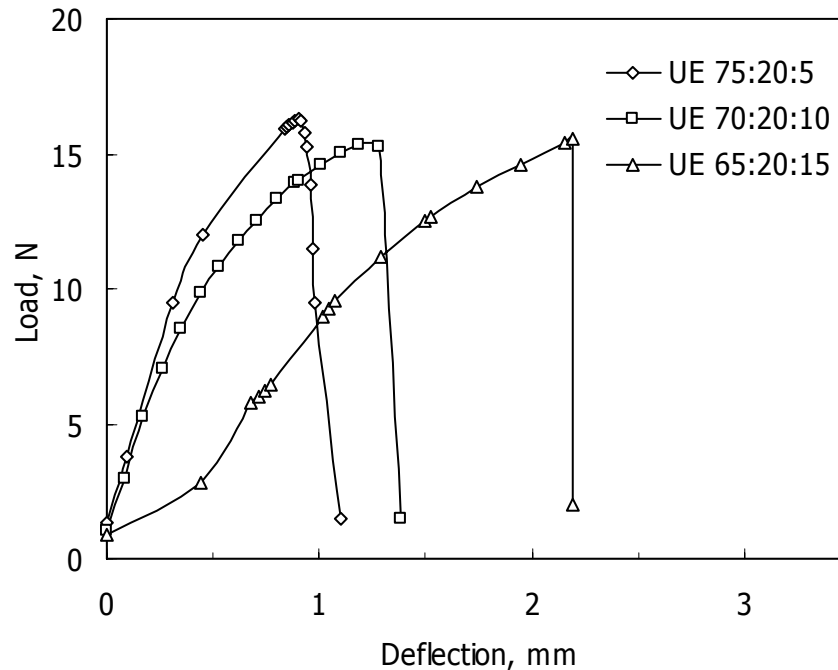
**Figure 45: Load deflection curve showing the effect of increasing the PVOH content on the mechanical properties of the urea-PVOH-based compounds**



**Figure 46: Load deflection curve showing the effect of increasing the wax content on the mechanical properties of the urea-PVOH-based compounds**



**Figure 47: Effect of varying EVA content on the load deflection curve of the EVA moulding compounds**



**Figure 48: Effect of varying wax content on the load deflection curve of the EVA moulding compounds**

The effect on the EVA and PVOH moulding compounds of increasing the wax and polymer contents was studied using load deflection curves. In the case of the PVOH moulding compounds, the effect of increasing the wax content from 5% to 15% at a constant PVOH content of 5% was studied. For the EVA moulding compound, the effect of increasing the polymer content at a constant wax content of 10% was studied. Lastly, the effect of increasing the wax content from 5% to 15% at a constant polymer content of 20% was studied.

As shown in Figure 45, a decrease in the PVOH content increases the maximum load and reduces the deflection to failure. This makes the moulding compounds strong but less tough i.e. change from ductile to brittle failure. This is because urea increases the stiffness in the polymer-filler matrix. This is seen at each degree of plasticisation. As shown in Figure 46, an increase in the wax content reduces the deflection to failure; this could be because the wax is crystalline and thus increases the stiffness.

As the degree of plasticisation (amount of glycerol) increases, the intermolecular friction between the PVOH molecules is reduced. This allows the molecules to slip and slide over each other more easily, thus reducing the rigidity of the PVOH and making it more flexible. An increase in the degree of plasticisation will therefore decrease the load at break (because there is less polymer) and increase the deflection at break.

As shown in Figure 47, as the EVA content is increased, the maximum load to failure decreases and the deflection increases. This produces moulding compounds that are less strong but tougher. This is because the increased EVA content provides greater flexibility and toughness.

As shown in Figure 48, an increase in the wax content does not affect maximum load but reduces the deflection. This polymer-filler interaction produces patterns that are strong but not tough.

**Table 17: Maximum Load and deflection point of PVOH moulding compounds**

<b>Urea:PVOH:wax</b>	<b>Maximum load (N)</b>	<b>Maximum Deflection (mm)</b>
90:5:5	79,6± 2,2	1,40± 0,12
85:10:5	61,7± 1,9	2,22± 0,36
80:15:5	60,8± 1,9	3,56± 0,13
85:5:10	81,6± 5,5	1,55 ± 0,27
80:5:15	81,2± 3,6	1,37 ± 0,28

**Table 18: Maximum Load and deflection point of EVA moulding compounds**

<b>Urea:EVA:wax</b>	<b>Maximum load (N)</b>	<b>Maximum Deflection (mm)</b>
75:20:5	16,8± 0,3	0,90± 0,06
80:10:10	29,9± 1,6	0,54± 0,02
70:20:10	21,2± 0,3	1,17± 0,09
60:30:10	11,6± 0,15	2,25± 0,03
65:20:15	17,1± 0,4	2,86±0,10

PVOH urea-based moulding compounds, on average, have loads-at-break several times greater than EVA-urea-based compounds. This is shown in Table 17 and 18. The deflection results show that the PVOH urea-based moulding compounds deflect less easily than the EVA-urea-based compounds. The type of polymer–filler interaction could explain this. In the case of the PVOH moulding compounds, there are strong hydrogen bonds between the OH group and the highly hydrophilic urea molecule, whereas in the case of the EVA moulding compounds there is weaker interaction between the acetate group and the urea molecules.

PVOH moulding compounds has superior mechanical properties compared with cooked PVOH moulding compound. This could be due to the breakdown of the compound as it is cooked above the urea degradation temperature of 132°C.

### **Flexural stress**

Flexural strength is also known as modulus of rupture, bending strength or fracture strength. The strength of a material in bending is expressed as the tensile stress on the outermost side of a bent test specimen, at the instant of failure. In flexural bending the sample is both in compression and tension. This is important as materials can fail in both tension and compression. This parameter determines the strength of a moulding compound to prevent any breakage during the assembly process of investment casting. The two-way ANOVA results obtained from the flexural stress experimental data are shown in Tables 19 to 21 below. The experimental data and the predicted data (linear regressed data) are then compared to establish a fit. The regression equations and the figures (Figures 49 to 51) are shown below.

**Table 19: Two-way ANOVA for flexural stress data for the urea-wax-PVOH compound containing 80 phr glycerol**

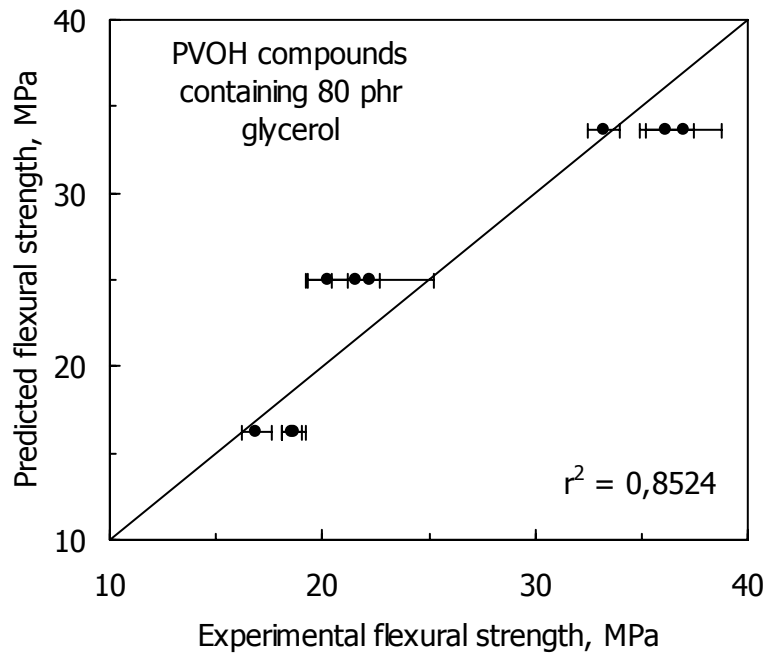
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	11,55	2	5,78	2,99	<0,0001
PVOH	2571,58	2	1285,79	665,84	<0,0001
Wax * PVOH	47,07	4	11,77	6,09	<0,0001
Error	69,72	36	1,93		
<i>Total</i>	<i>2699,72</i>	<i>44</i>			

**Table 20: Two-way ANOVA for flexural stress data for the urea-wax-PVOH compound containing 40 phr glycerol**

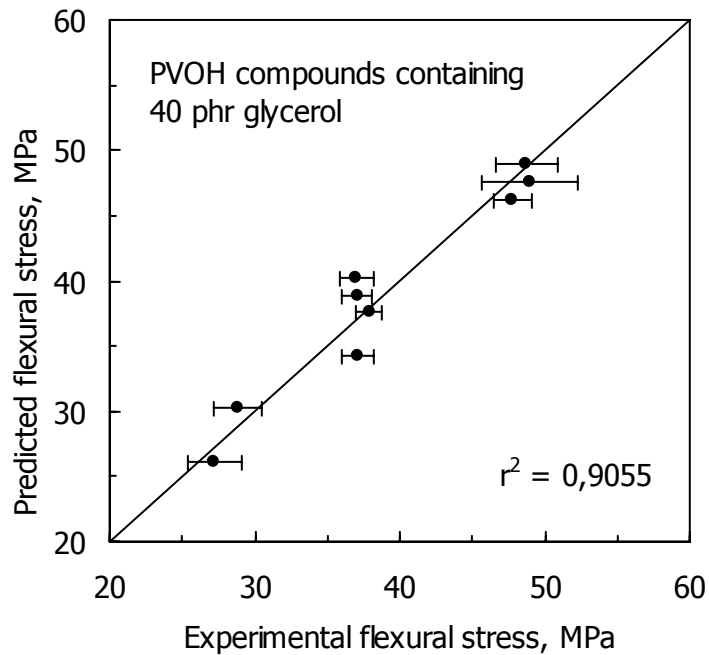
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	64,13	2	32,07	10,28	<0,0001
PVOH	2335,95	2	1167,98	374,56	<0,0001
Wax * PVOH	222,63	4	55,66	17,85	<0,0001
Error	112,26	36	3,12		
<i>Total</i>	<i>2734,97</i>	<i>44</i>			

**Table 21: Two-way ANOVA for flexural stress data for the urea-EVA-wax compounds**

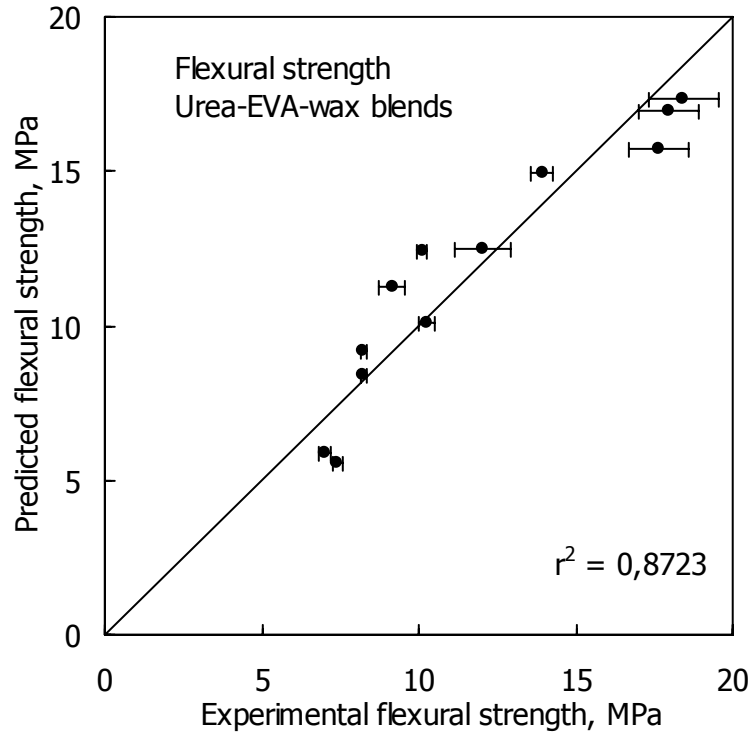
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	115,45	2	57,725	164,09	<0,0001
EVA	822,12	5	164,425	467,38	<0,0001
Wax * EVA	64,76	4	16,191	46,02	<0,0001
Error	16,89	48	0,352		
<i>Total</i>	<i>1019,22</i>	<i>59</i>			



**Figure 49: Comparison between predicted and experimental flexural stress data for linear model fit of the urea-wax-PVOH (80 phr glycerol) compound**



**Figure 50: Comparison between predicted and experimental flexural stress for a linear model fit of UP4 data**



**Figure 51: Comparison between predicted and experimental flexural stress for linear model fit of urea EVA-wax data**

### Data analysis

The two-way ANOVA result for the PVOH urea-based moulding compounds containing 80 phr and 40 phr glycerol, and the EVA compounds are shown in Tables 19 to 21. It is concluded that the polymer, the wax and their interaction are significant in all three cases. The regression yields:

PVOH (80 phr glycerol):

$$Y_{Flexural\ stress} = 38,17 + 42,10 X_{wax} - 143,95 X_{PVOH} - 303,80 X_{wax} X_{PVOH} \quad (r^2 = 0,8512) \quad (34)$$

PVOH (40 phr glycerol):

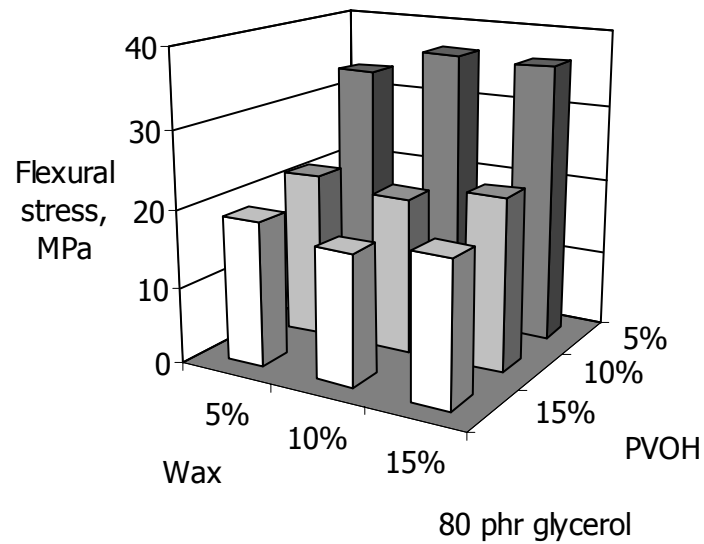
$$Y_{Flexural\ stress} = 48,2 - 65,9 X_{wax} + 81,4 X_{PVOH} - 1083,1 X_{wax} X_{PVOH} \quad (r^2 = 0,7714) \quad (35)$$

Urea-EVA-wax:

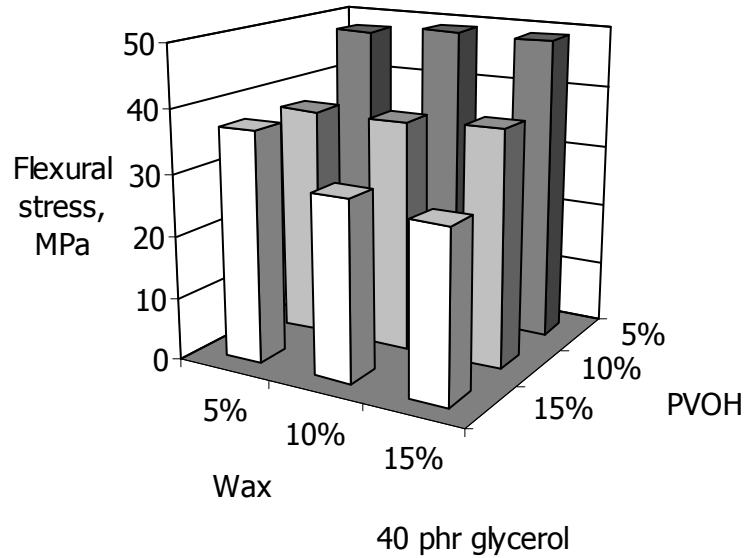
$$Y_{Flexural\ stress} = 28,40 - 73,91 X_{wax} - 57,60 X_{EVA} + 170,94 X_{wax} X_{EVA} \quad (r^2 = 0,8723) \quad (36)$$



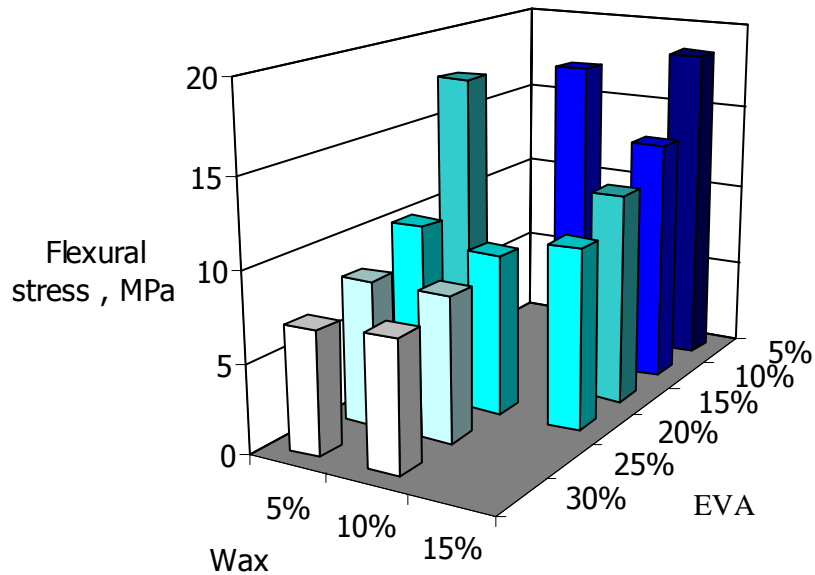
In the case of the EVA and urea-wax-PVOH (80 phr glycerol), the model fits with over 85% of the total variation in the data about the average explained. A poor fit with only 77% total variation in the data about the average explained was shown by the urea-wax-PVOH (40 phr) moulding compounds. The average results of the data analysed are depicted in Figures 52 to 54 below.



**Figure 52: Flexural stress of the urea-wax-PVOH (80 phr glycerol) compound**



**Figure 53: Flexural stress of the urea-wax-PVOH (40 phr glycerol) compound**



**Figure 54: Flexural stress of the urea-EVA-wax compound**

At any degree of plasticisation, the flexural stress increases as the polymer content is reduced, as shown in Figures 52 and 53. This is attributed to increases in stiffness as the urea content is increased. Increasing the wax content does not affect the flexural strength to a large extent at any degree of plasticisation. This could be because the wax and PVOH do not form a compatible blend.

As the degree of plasticisation decreases from 80 phr to 40 phr, the intermolecular friction between the PVOH molecules increases, causing the molecules to slip and slide over each other less easily. This increases the rigidity of the PVOH, making it less flexible and increasing the tensile strength and the flexural stress.

The flexural stress data for the EVA moulding compounds are shown in Figure 54. As the EVA content is increased, the flexural stress decreases. This could be explained by the effect of the reduction in the urea content, which is associated with a loss of stiffness. The flexural stress varies little with the wax content.

The PVOH moulding compounds had superior flexural stress compared with the EVA moulding compounds because of strong hydrogen bonding between the urea and the hydroxyl group of the PVOH. In contrast, in the case of the EVA moulding compounds there is a weak bonding interaction between the acetate group (hydrophobic) of the EVA/wax blend and the urea.

The flexural stress of the industrial cooked urea moulding compound (benchmark) was weaker than that of the PVOH moulding compound prepared with a two-roll mill. This could be due to the degradation of the urea as it is cooked above its degradation temperature of 132°C.

### **Flexural strain**

Flexural strain provides a measure of the flexibility of a material. Higher strain-at-break indicates superior flexibility. Excessive flexibility can affect the dimensional stability of moulding patterns during the assembly process in investment casting. Two-way ANOVA was used to analyse the flexural strain results for the urea-based moulding compounds. The results obtained are shown in Tables 22 to 24 below. The experimental data and the predicted data (linear regressed data) are compared in Figures 55 to 57. The regression equations are also given below.

**Table 22: Two-way ANOVA for flexural strain of the urea-PVOH-wax compound containing 80 phr glycerol**

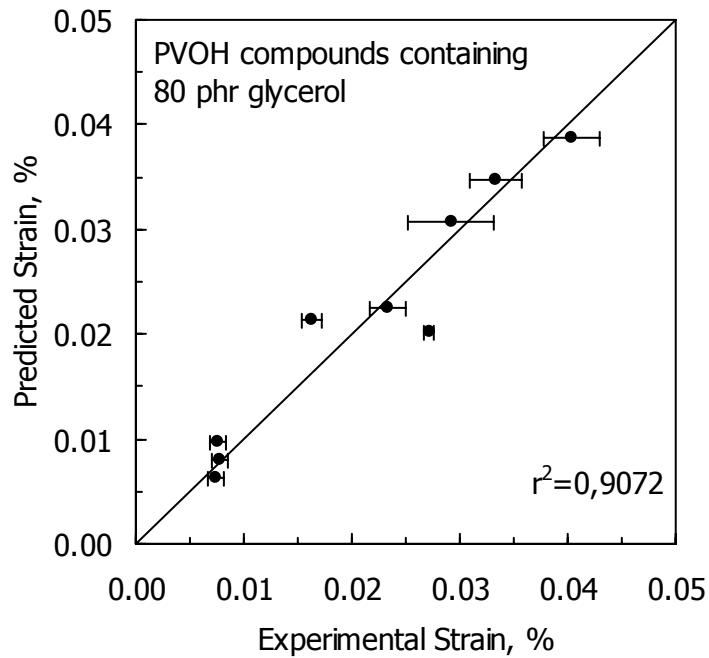
<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	0,00016	2	0,00008	21	< 0.001
PVOH	0,00536	2	0,00268	723	< 0.001
Wax*PVOH	0,00047	8	0,00012	32	< 0.001
Error	0,00013	30			
<i>Total</i>	<i>0,00612</i>	<i>44</i>			

**Table 23: Two-way ANOVA for flexural strain of the urea-PVOH-wax compound containing 40 phr glycerol**

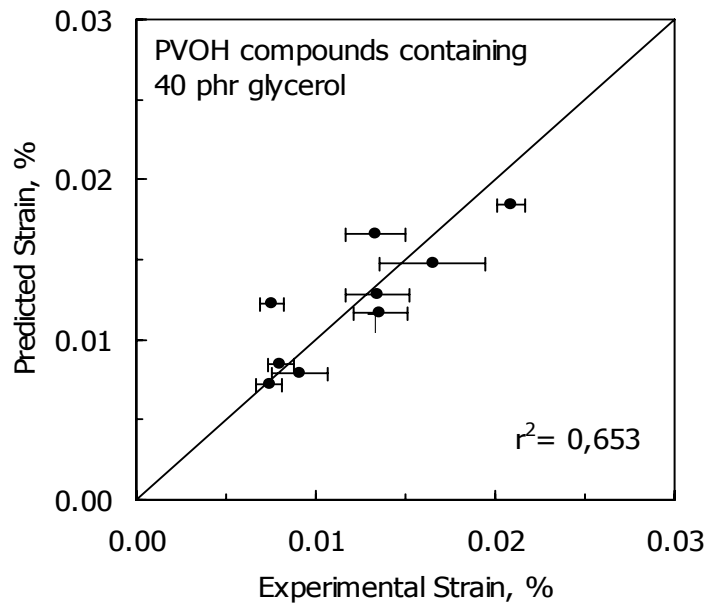
<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	0,00012	2	0,00006	25	< 0.001
PVOH	0,00058	2	0,00029	121,1	< 0.001
Wax*PVOH	0,00015	8	0,00004	15,52	< 0.001
Error	0,00009	30			
<i>Total</i>	<i>0,00094</i>	<i>44</i>			

**Table 24: Two-way ANOVA for flexural strain of the urea-EVA-wax compounds**

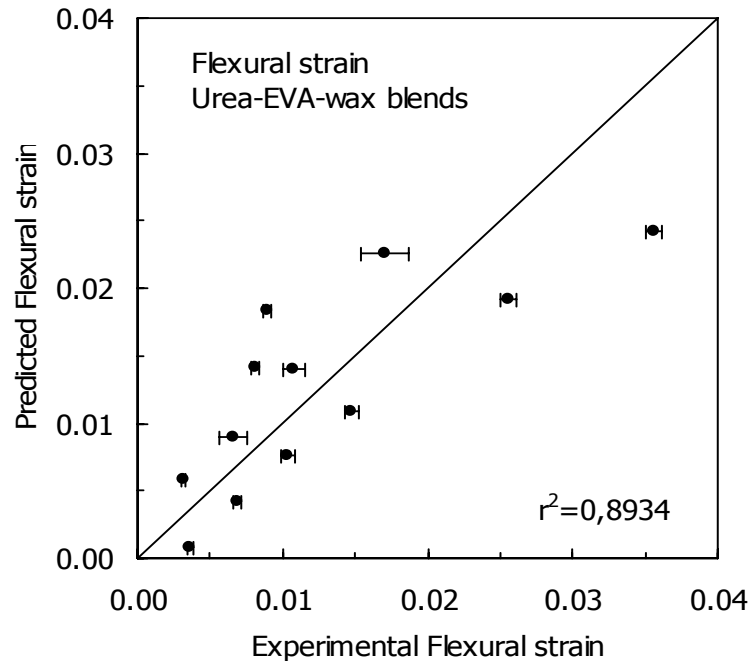
<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	0,00148	2	0,00074	1509,6	0
EVA	0,00296	5	0,00059	1211,3	0
Wax*EVA	0,00057	4	0,00014	292.1	0
Error	0,00002	48			
<i>Total</i>	<i>0,00504</i>	<i>59</i>			



**Figure 55: Comparison between predicted and experimental flexural strain for linear model fit of the urea-wax-PVOH (80 phr glycerol) compound data**



**Figure 56: Comparison between predicted and experimental flexural strain for linear model fit of the urea-wax-PVOH (40 phr glycerol) compound data**



**Figure 57: Comparison between predicted and experimental flexural strain for linear model fit of the urea-EVA-wax compound data**

### Data analysis

The two-way ANOVA results for the PVOH urea-based compounds containing 80 phr and 40 phr glycerol, and for the EVA compounds, are shown in Tables 22 to 24. From the results, the polymer and the waxes, and their interaction, are significant for all the moulding compounds. The linear regression leads to:

PVOH (80 phr glycerol):

$$Y_{Flexural\ strain} = -0,0144 + 0,3815 X_{PVOH} + 0,0908 X_{wax} - 1,1455 X_{wax} X_{PVOH} \quad (r^2 = 0,9027) \quad (37)$$

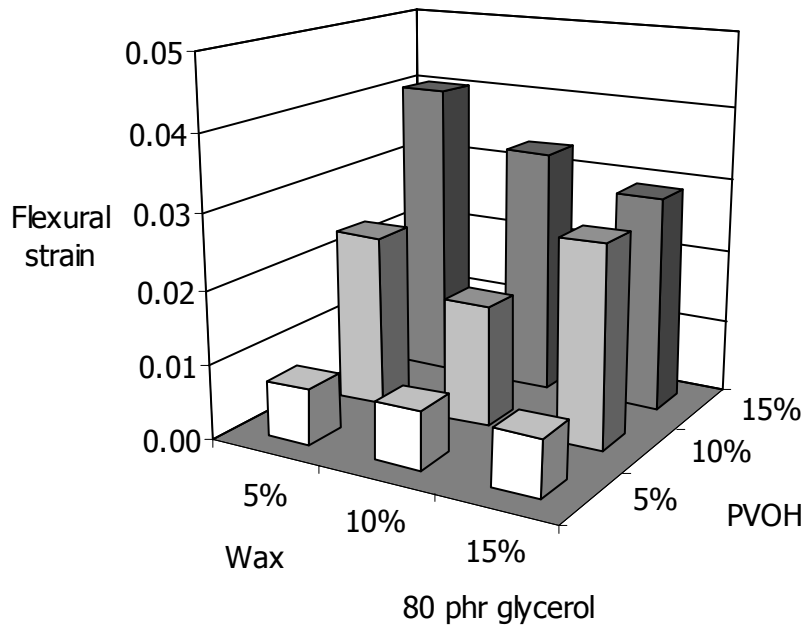
PVOH (40 phr glycerol):

$$Y_{flexural\ strain} = -0,0003 + 0,1370 X_{PVOH} + 0,0379 X_{wax} - 0,4972 X_{wax} X_{PVOH} \quad (r^2 = 0,653) \quad (38)$$

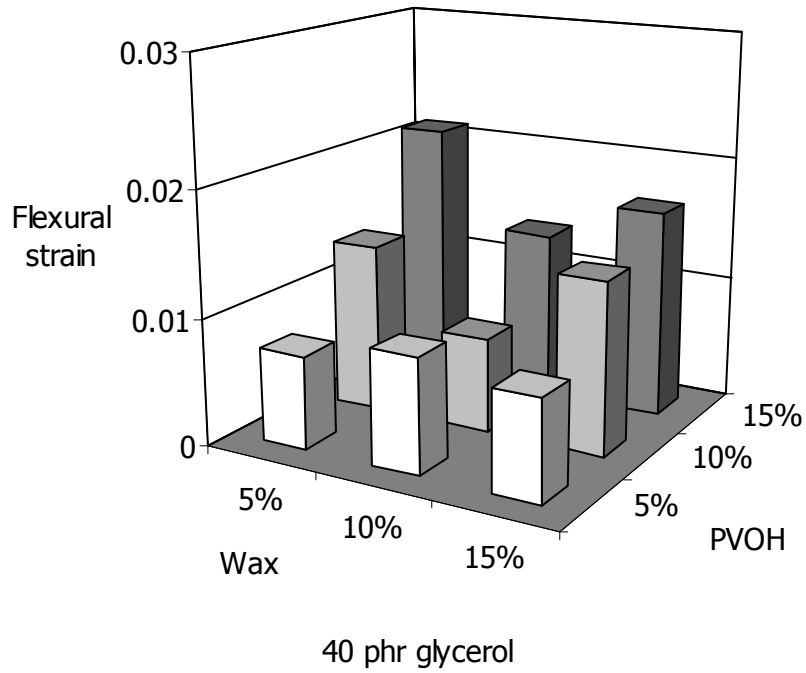
Urea-EVA-wax:

$$Y_{Flexural\ strain} = -0,0158 + 0,050 X_{EVA} + 0,1317 X_{wax} + 0,341 X_{wax} X_{EVA} \quad (r^2 = 0,893) \quad (39)$$

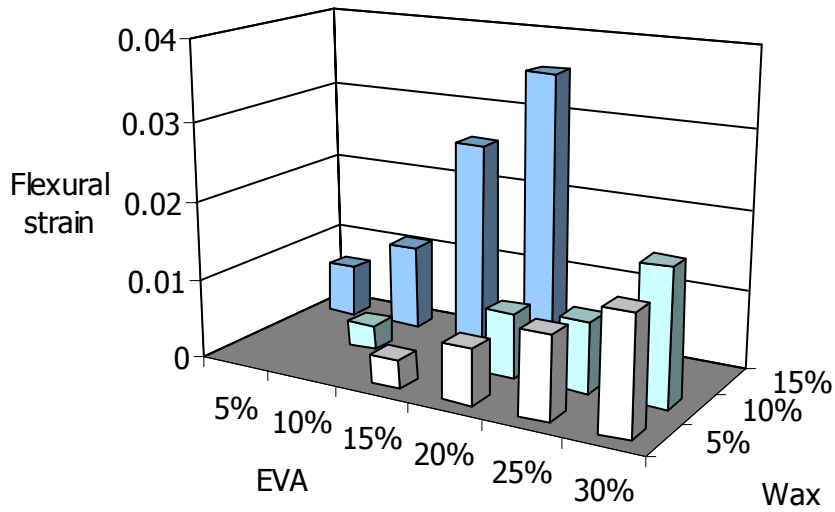
The results of the data analysed are depicted in Figures 58 to 60 below. In the case of both the EVA and the urea-wax-PVOH (80 phr glycerol) compounds, the model fits well. A poor fit was obtained with the urea-wax-PVOH (40 phr) compound: the linear model only explains 65% of the total variation in the data about the average. Indeed, Figure 56 shows that the response is non-linear.



**Figure 58: Flexural strain of the urea-wax-PVOH (80 phr glycerol) compound**



**Figure 59: Flexural strain of the urea-wax-PVOH (40 phr glycerol) compound**



**Figure 60: Flexural strain of the urea-EVA-wax compound**



The results given in Figures 58 and 59 shows that as the PVOH content is increased, the flexural strain increases as expected for both degrees of plasticisation.

An increase in the wax content slightly affects the flexural strain at any degree of plasticisation. This is because PVOH is highly hydrophilic and wax is hydrophobic and therefore they will resist each other. A decrease in the degree of plasticisation from 80 to 40 phr reduces the flexural strain and vice versa. Based on the definition of plasticisation, the elongation should increase with an increase in the plasticiser concentration. This is because the intermolecular attraction between polymer chains gets weaker as the glycerol content is increased due to the increase in free volume. This improves the flexibility of the PVOH chains, thus increasing the flexural strain. As shown in Figure 60, the flexural strain increases as the EVA content is increased, as expected. An increase in the wax content also increases the flexural strain slightly. This could be explained by the fact that wax forms a compatible blend with EVA.

The flexural strain data show that the PVOH urea-based compounds have greater flexural strain compared with the EVA-urea-based compounds at a given urea content. This could be explained by the type of urea and polymer interactions that occur. The superior flexural strain obtained with the PVOH moulding compounds, compared to the EVA moulding compounds, may be attributed to better compatibility of this polymer with urea through hydrogen bonding interactions and also to the higher molecular mass of this polymer.

The flexural strain of the industrial cooked urea-moulding compound (benchmark) was higher than that of the PVOH and EVA moulding compounds. This could be due to urea's loss of stiffness as it is cooked above its degradation temperature of 132°C.

### **Fracture energy**

The Charpy impact test provides quantitative information on the material behaviour at a very high strain rate (brittle fracture). In contrast, the process of breaking the sample in a three-point bending test provides information on the fracture energy at low strain rates. The moulding compounds studied here showed mostly brittle fracture behaviour. In brittle fracture, the fracture energy equals the work done during the breaking of a sample. It corresponds to the area under a load-versus-deflection curve. The two-way ANOVA results obtained from the

flexural stress experimental data are shown in Tables 25 to 27 below. The experimental data and the predicted data (linear regressed data) are then compared to establish a fit. The regression equations are also given below.

**Table 25: Two-way ANOVA for fracture energy of the urea-PVOH-wax compounds containing 80 phr glycerol**

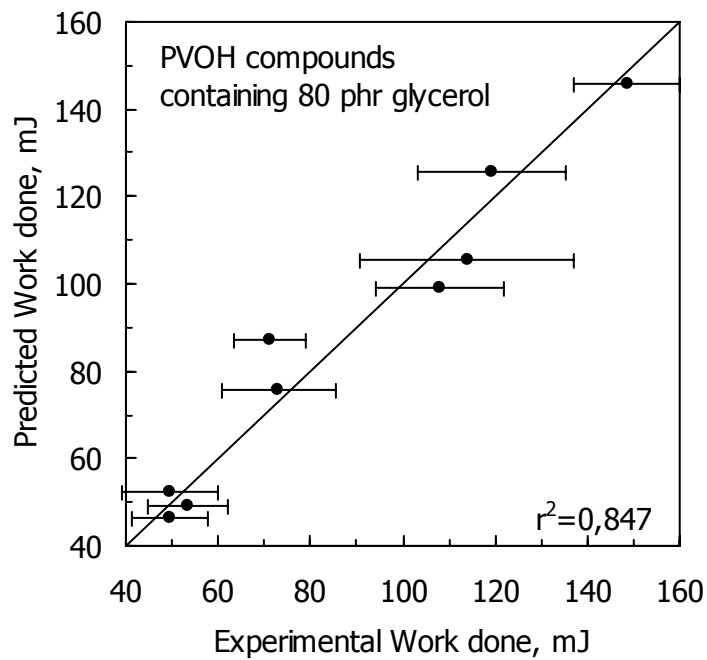
<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	4 858	2	2 429	13,82	< 0,0001
PVOH	44 000	2	22 000	125,2	< 0,0001
Wax*PVOH	2 958	8	739,4	4,21	0,0068
Error	6 328	30	175,8		
<i>Total</i>	<i>58 145</i>	<i>44</i>			

**Table 26: Two-way ANOVA for fracture energy of the urea-PVOH-wax compounds containing 40 phr glycerol**

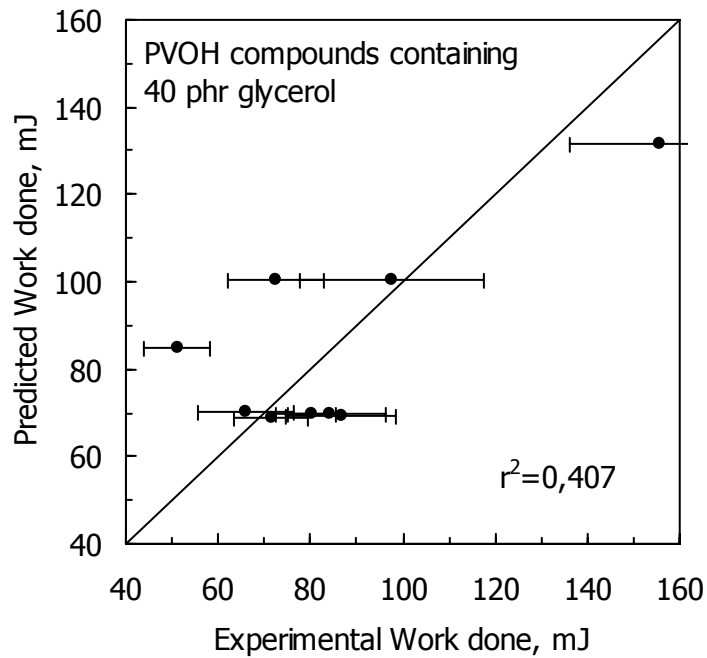
<b>Source</b>	<b>Sum-of-squares</b>	<b>Degrees of freedom</b>	<b>Mean square</b>	<b>F</b>	<b>Probability &gt; F</b>
Wax	12 544	2	6272	39,6	< 0,0001
PVOH	8 854	2	4 417,8	27,89	< 0,0001
Wax*PVOH	13 606	8	3 401,4	21,47	< 0,0001
<i>Error</i>	<i>5 702</i>	<i>30</i>	<i>158,4</i>		
<i>Total</i>	<i>40 687</i>	<i>44</i>			

**Table 27: Two-way ANOVA for Fracture energy urea-EVA-wax compounds**

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	17	2	8,677	8,42	0,0007
EVA	1 598	2	319,6	310,27	< 0,0001
Wax*EVA	34	8	8,586	8,34	< 0,0001
Error	49	30	1,030		
<i>Total</i>	<i>1 699</i>	<i>44</i>			



**Figure 61: Comparison between predicted and experimental fracture energy for quadratic model fit of the urea-wax-PVOH (80 phr glycerol) compound data**



**Figure 62: Comparison between predicted and experimental fracture energy for quadratic model fit of UP4 data**

### Data analysis

The two-way ANOVA results for the PVOH urea-based compounds containing 80 phr and 40 phr glycerol, and for the EVA compounds, are shown in Tables 25 to 27. It is concluded that both the polymer and the wax, and their interaction, are significant in all three cases. Regression yields:

PVOH (80 phr glycerol):

$$Y_{Fracture\ energy} = -0,3 + 1108,8 X_{PVOH} + 113,2 X_{wax} - 3451,0 X_{wax} X_{PVOH} \quad (r^2 = 0,840) \quad (40)$$

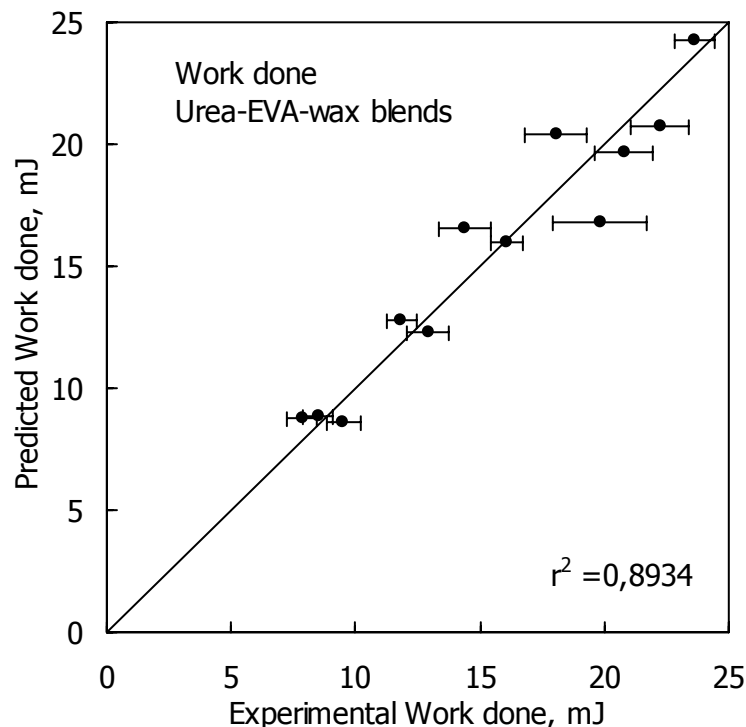
PVOH (40 phr glycerol):

$$Y_{fracture\ energy} = 21,20 + 943,7 X_{PVOH} + 330,2 X_{wax} - 6353,2 X_{wax} X_{PVOH} \quad (r^2 = 0,4709) \quad (41)$$

Urea-EVA-wax:

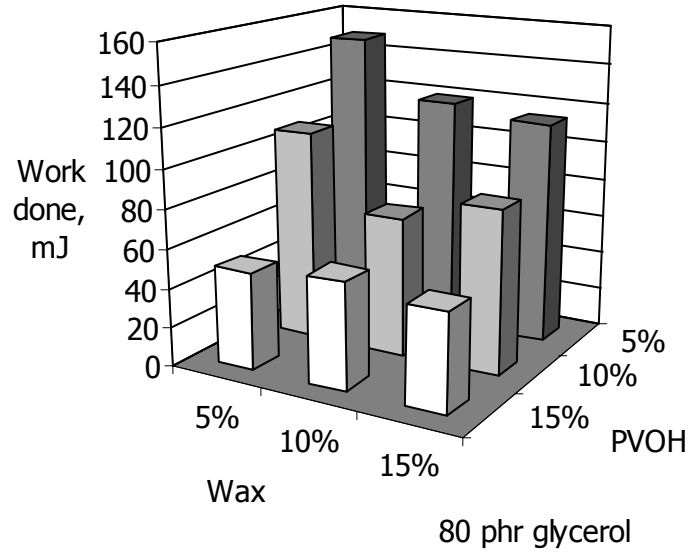
$$Y_{Fracture\ energy} = -6,00 + 71,49 X_{EVA} + 70,32 X_{wax} + 66.536 X_{wax} X_{EVA} \quad (r^2 = 0,8934) \quad (42)$$

In the case of the EVA compound and the urea-wax-PVOH (80 phr glycerol) compound, the model fits with over 85% of the total variation in the data about the average explained. The poor fit seen for the PVOH (40 phr) compound is attributed to the non-linear response evident in Figure 62. The average results of the data analysed are shown in Figures 64 to 66 below.

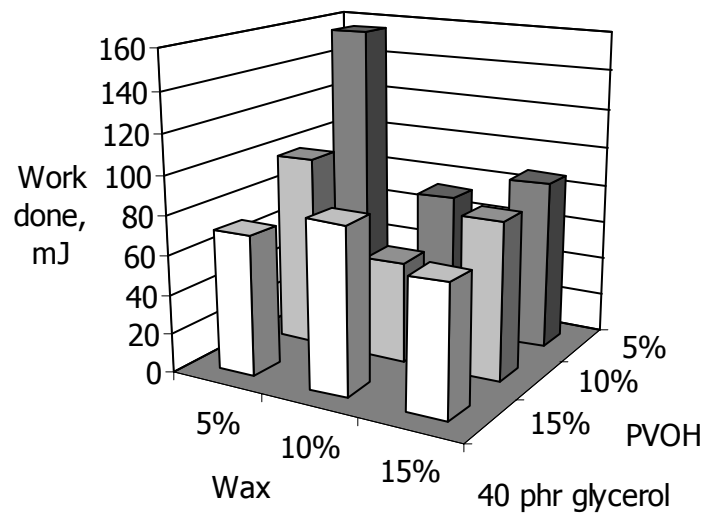


**Figure 63: Comparison between predicted and experimental fracture energy for linear model fit of urea-EVA-wax compound data**

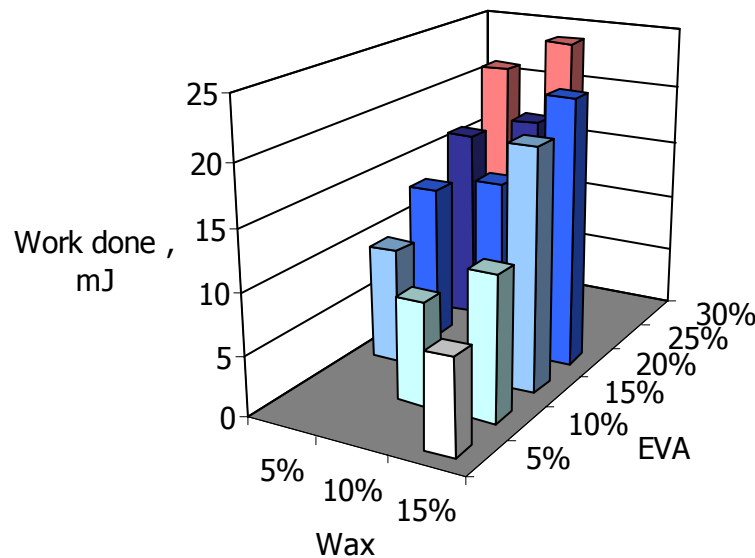
Figures 64 and 65 confirm that the work done to fracture increases with an increase in the polymer content. This is true irrespective of the degree of plasticisation and implies that the polymer reinforces the urea compound (or increases the ductility which will increase the area under the curve). The microscopic mechanism is not known. However, it may be that the polymer acts as a binder for the urea crystallites i.e. changing from brittle to ductile fracture behaviour.



**Figure 64: Fracture energy of the urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 65: Fracture energy of the urea-wax-PVOH (40 phr glycerol) compounds**



**Figure 66: Fracture energy of the urea-EVA-wax compounds**

The effect of the wax does depend on the degree of plasticisation. This could be because an increased wax content increases the stiffness and crystallinity slightly, causing a reduction in the deflection point. Since PVOH is highly hydrophilic and wax is hydrophobic, there is little interaction between them. The wax merely acts as an external lubricant to eliminate external friction between the polymer and the metal surface of the processing equipment.

As the degree of plasticisation of the PVOH is increased from 40 to 80 phr, the fracture energy of the urea moulding compound increases. Thus PVOH urea-based compounds containing 80 phr glycerol are tougher. This correlates with the lower glass transition temperature ( $T_g$ ) for this polymer, i.e. it relates to the theory behind plasticisation. As the amount of glycerol increases, there is a reduction in the intermolecular friction between the polymer molecules, so the molecules can slip and slide over each other more easily, producing a more flexible polymer. This causes the elongation to increase and hence improves the fracture energy (toughness).

The results for the EVA moulding compounds are shown in Figure 66. As the polymer content is increased, a higher value of fracture energy is expected. When the polymer content is increased, flexibility is increased, causing the moulding compound to undergo a greater deflection to break. This is clearly depicted in an increase in the area under the load and deflection point. As the wax content is increased, the fracture energy increases. This shows that the wax acts merely as an internal lubricant, forming a compatible blend with the EVA matrix and thus enhancing the toughness of the EVA urea-based moulding compounds.

The fracture energy shows that the PVOH urea-based moulding compounds are about seven times tougher than the EVA-urea compounds. This depends largely on the urea-polymer interaction. Urea is a hydrophilic organic compound and therefore forms strong hydrogen bonds with the hydroxyl group of plasticised PVOH. The acetate group is highly hydrophobic and therefore interacts weakly with the hydrophilic urea.

The results in Appendix A show that the industrial cooked urea-based compound (benchmark) is not as tough as the PVOH urea-based moulding compounds prepared via the conventional two-roll mill process.

### **Modulus of elasticity**

The modulus of elasticity provides information about the degree of stiffness of a material. The stiffness of a material corresponds to the gradient of the straight line in the load-versus-deflection curve. The modulus of elasticity increases as the slope becomes steeper. The two-way ANOVA results obtained from the flexural stress experimental data are shown in Tables 28 to 30 below. The experimental data and the predicted data (linear regressed data) are then compared in Figures 66 to 68 to establish a fit. The regression equations are also given below.



**Table 28: Two-way ANOVA for the modulus of elasticity of the urea-PVOH-wax compounds containing 80 phr glycerol**

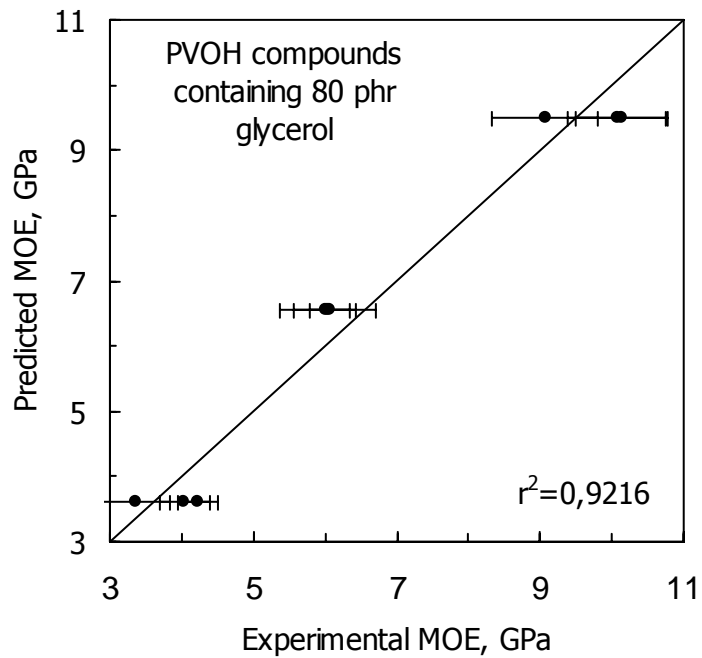
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	1,302	2	0,6508	0,61	0,552
PVOH	244,312	2	61,078	56,88	0
Wax*PVOH	3,665	8	0,4581	0,43	0,8957
Error	32,213	30	1.0738		
<i>Total</i>	<i>281,492</i>	<i>44</i>			

**Table 29: Two-way ANOVA for the modulus of elasticity of the urea-PVOH-wax compounds containing 40 phr glycerol**

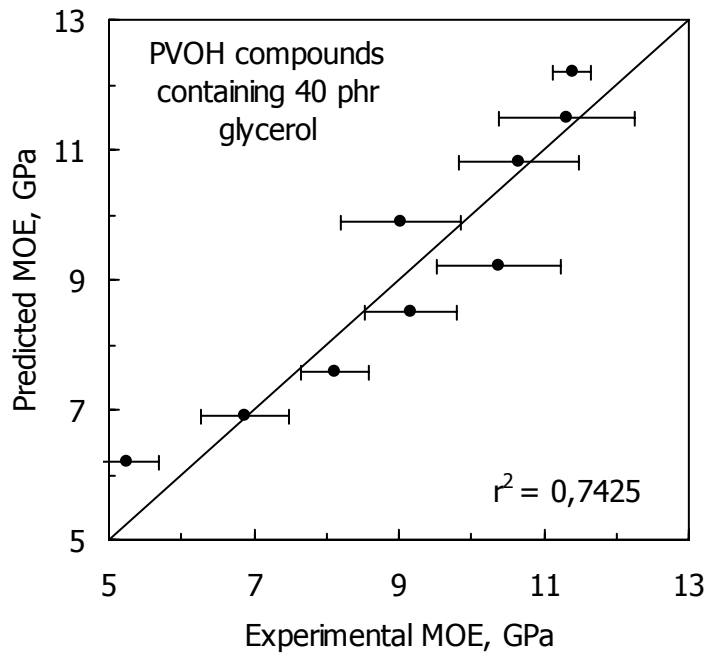
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	13,616	2	6,8082	6,55	0,0044
PVOH	127,850	2	31,9624	30,74	0
Wax*PVOH	18,577	8	2,3221	2,23	0,0531
Error	31,193	30	1,0398		
<i>Total</i>	<i>191,236</i>	<i>44</i>			

**Table 30: Two-way ANOVA for the modulus of elasticity of the urea-EVA-wax compounds**

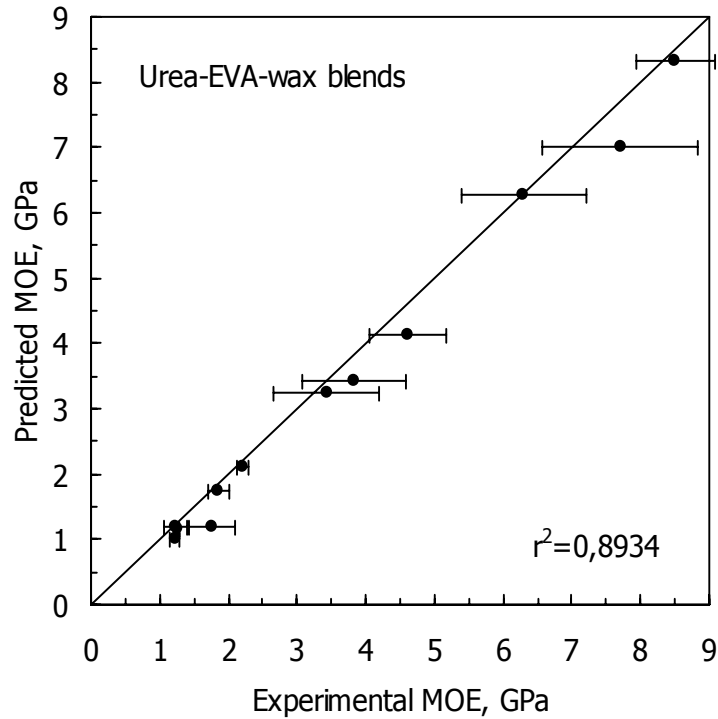
Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	115,5	2	57,73	164,09	< 0,0001
EVA	822,12	5	164,43	476,4	< 0,0001
EVA*Wax	64,7	4	16,2	46,0	< 0,0001
Error	16,9	48	0,35		
<i>Total</i>	<i>1019,22</i>	<i>59</i>			



**Figure 67: Comparison between the predicted and experimental modulus of elasticity for quadratic model fit of urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 68: Comparison between predicted and experimental modulus of elasticity for quadratic model fit of urea-wax-PVOH (40 phr glycerol) compounds**



**Figure 69: Comparison between predicted and experimental modulus of elasticity for quadratic model fit of urea EVA-wax compounds**

**Data analysis**

It is concluded that both the polymer and the wax, and their interaction, are significant in all three cases. Regression yields:

PVOH (80 phr glycerol):

$$Y_{MOE} = -1,4644 + 54,04 X_{PVOH} + 6,973 X_{wax} - 260,0 X_{wax} X_{PVOH} \quad (r^2 = 0,9216) \quad (43)$$

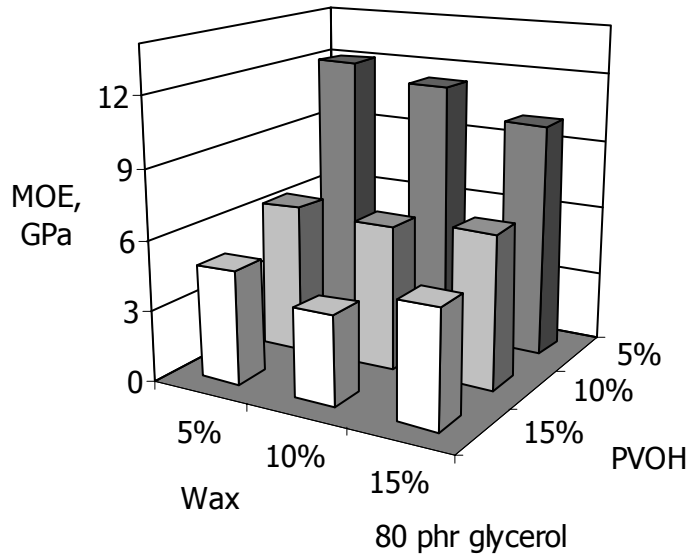
PVOH (40 phr glycerol):

$$Y_{MOE} = 12,53 + -22,35 X_{PVOH} + 9,75 X_{wax} - 213,80 X_{wax} X_{PVOH} \quad (r^2 = 0,7425) \quad (44)$$

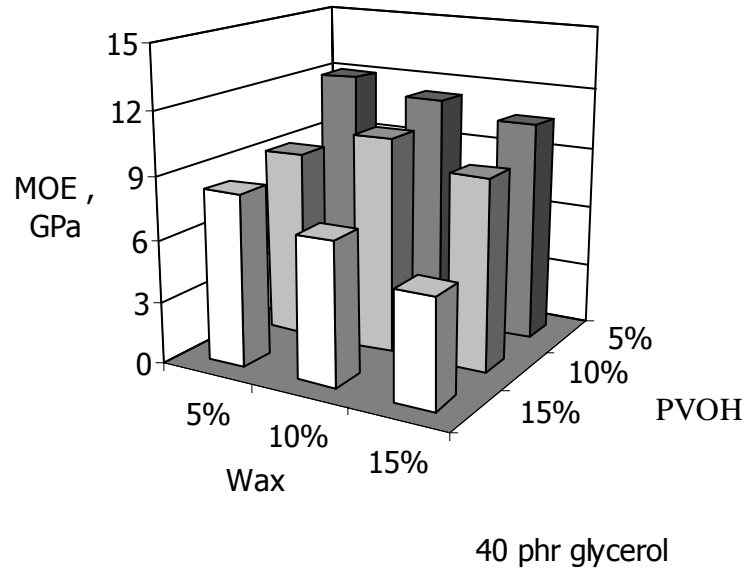
Urea-EVA-wax:

$$Y_{MOE} = -6,00 + 71,49 X_{EVA} + 70,32 X_{wax} + 66.536 X_{wax} X_{EVA} \quad (r^2 = 0,8934) \quad (45)$$

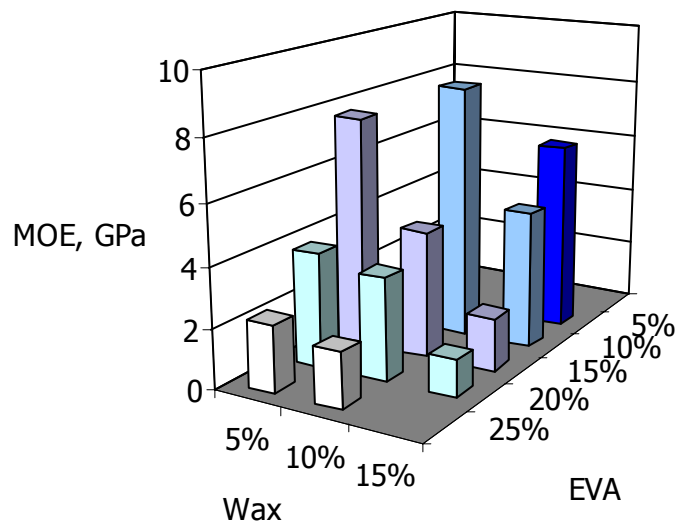
The poor fit seen for the PVOH with 40 phr glycerol is attributed to the non-linear response evident in Figure 68.



**Figure 70: Modulus of elasticity of the urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 71: Modulus of elasticity of the urea-wax-PVOH (40 phr glycerol) compounds**



**Figure 72: Modulus of elasticity of the urea-EVA-wax compounds**

At any degree of plasticisation the modulus of elasticity increases as the polymer content is decreased, as shown in Figures 70 and 71. This is attributed to increases in stiffness as the urea content is increased. Increasing the wax content affects the modulus of elasticity to a small extent at any degree of plasticisation. This could be because the wax and the PVOH do not form any compatible blend. The PVOH is highly hydrophilic and the wax is hydrophobic and therefore they will resist each other.

Increasing the glycerol content in the PVOH from 40 to 80 phr decreased the modulus of elasticity. This is because the tensile strength is reduced and the percentage of elongation is increased.

The modulus of elasticity data for the EVA compounds is shown in Figure 72. As the EVA and wax contents are increased, the modulus of elasticity falls. Firstly, this could be explained by the effect of reducing the urea content, which reduces stiffness. Secondly, wax and EVA form compatible blends, which will contribute to the same effect.

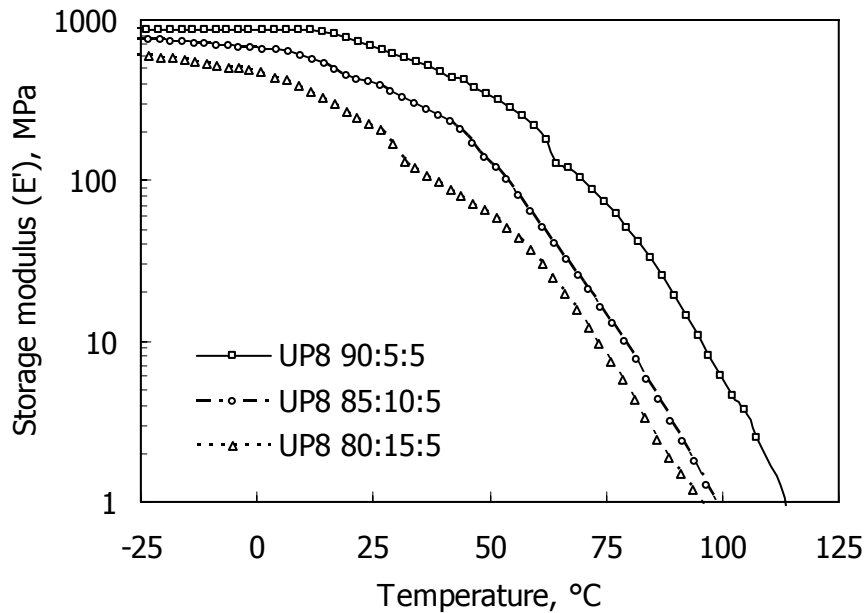
The modulus of elasticity of the PVOH urea-based moulding compounds is approximately double that of the EVA moulding compounds at a given urea content. This could be explained by the type of filler used and by the polymer interactions that take place. PVOH forms strong hydrogen bonds with urea because of the presence of the hydroxyl group, whereas in the EVA moulding compounds there is only a weak interaction between the hydrophobic acetate group and urea.

The PVOH moulding compounds have superior moduli of elasticity compared with the cooked urea-based compound. This could be explained by the fact that the cooking process destroys the structural properties of urea when it is heated above its degradation temperature.

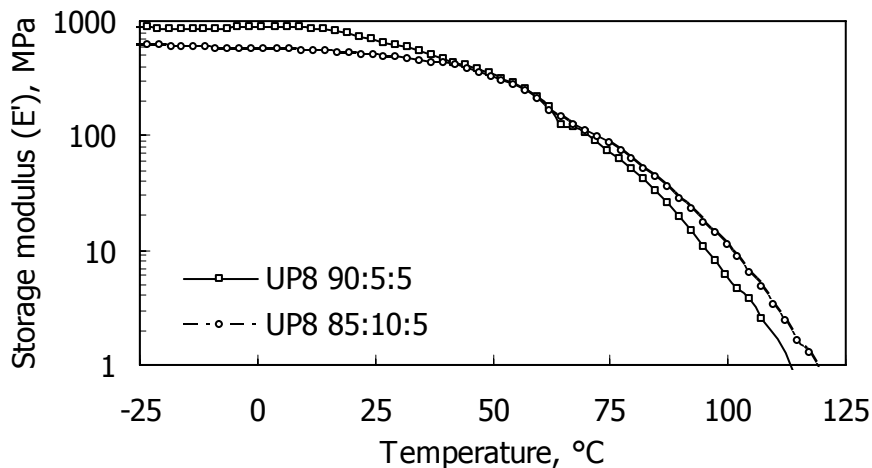
#### **8.4 Dynamic mechanical analysis**

Polymers are viscoelastic materials, i.e. they exhibit properties characteristic of viscous liquids and elastic solids. The mechanical properties of polymers depend on temperature. They are also time-dependent. This temperature-time-dependent relaxation behaviour can be studied using the stress-strain relationship generated by dynamic mechanical analysis (DMA). The main

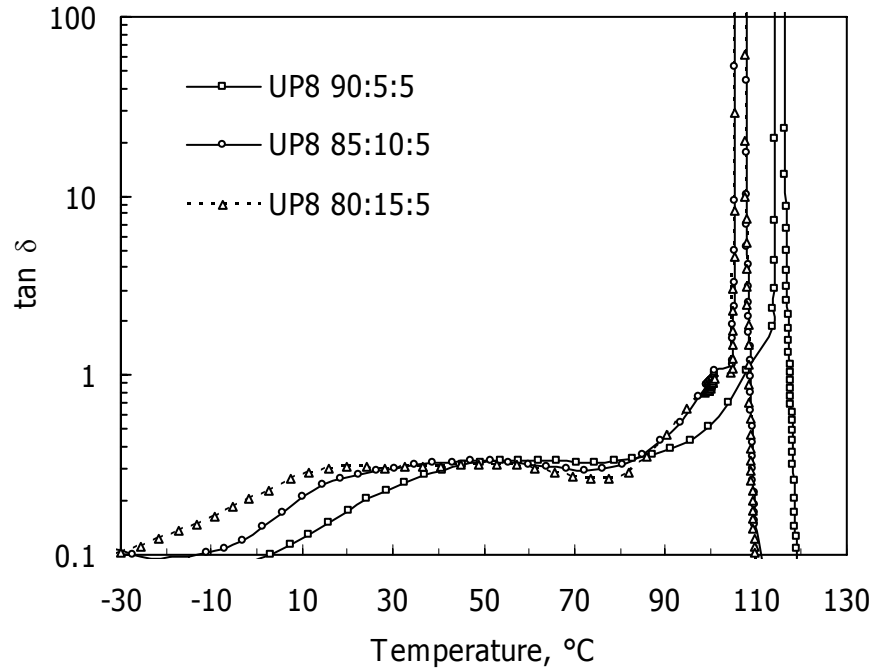
variables measured in DMA are the storage modulus ( $E'$ ), which represents the elastic modulus; the loss modulus ( $E''$ ) representing the viscous component, and the damping factor ( $\tan(\delta)$ ), defined as the ratio of  $E''/E'$ . The experimentally determined dynamic mechanical behaviours of the urea-based moulding compounds are depicted in Figures 73 to 80.



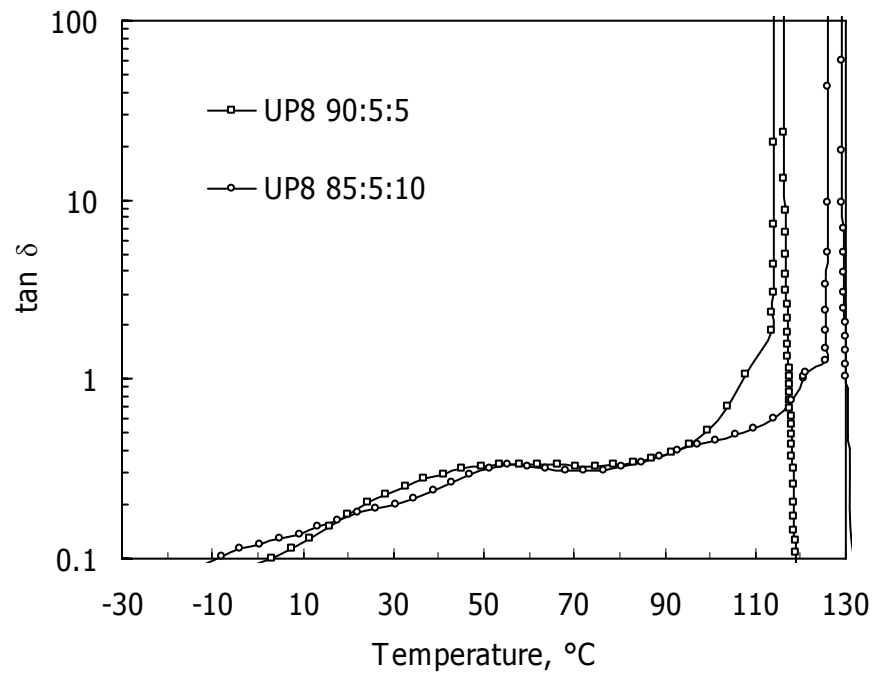
**Figure 73: Effect of increasing the polymer content on the storage modulus versus the temperature of the urea-PVOH moulding compounds**



**Figure 74: Effect of increasing the wax content on the storage modulus versus the temperature of the urea-PVOH moulding compounds**

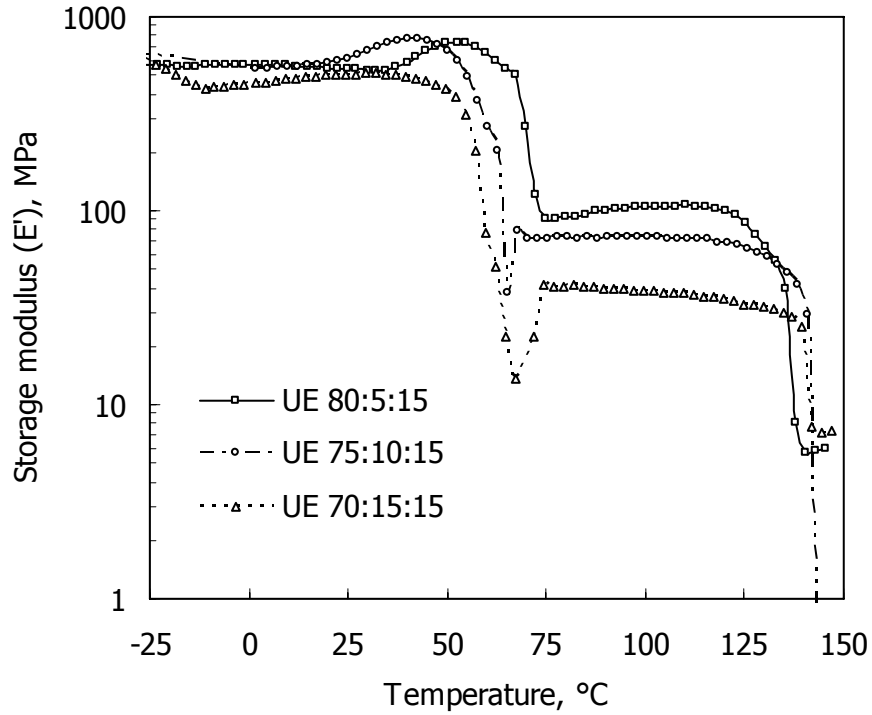


**Figure 75: Effect of increasing the polymer content on the damping factor versus the temperature of the urea-PVOH moulding compounds**

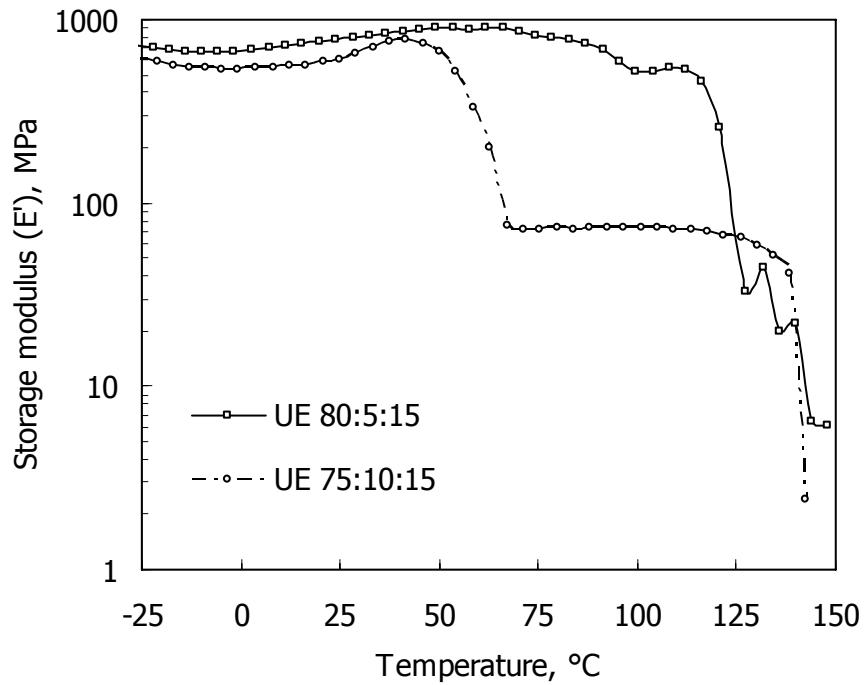


**Figure 76: Effect of increasing the wax content on the damping factor versus the temperature of the urea-PVOH moulding compounds**

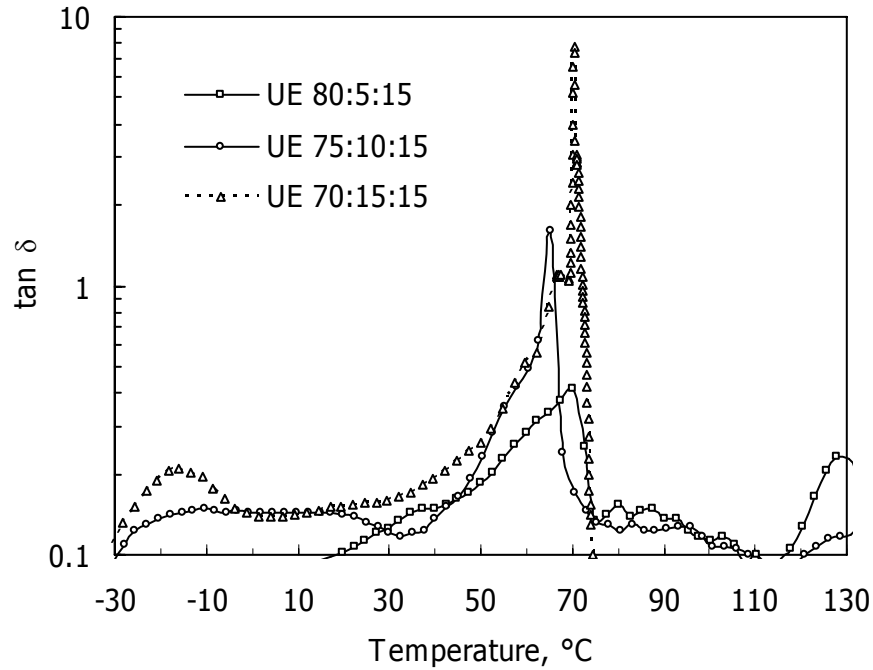




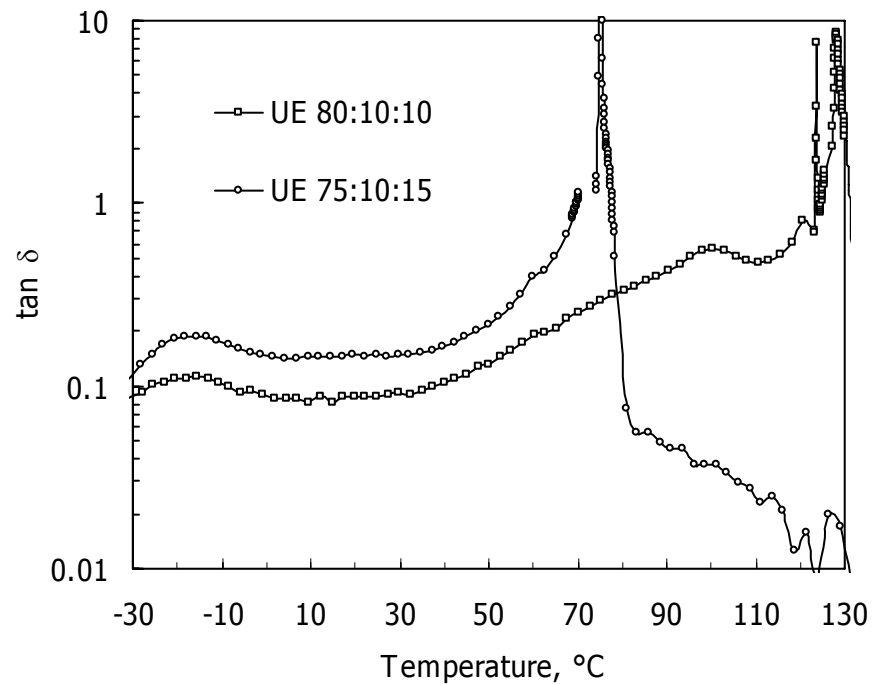
**Figure 77: Effect of increasing the polymer content on the storage modulus versus the temperature of the urea-EVA moulding compounds**



**Figure 78: Effect of increasing the wax content on the storage modulus versus the temperature of the urea-EVA moulding compounds**



**Figure 79: Effect of increasing the polymer content on the damping factor versus the temperature of the urea-EVA moulding compounds**



**Figure 80: Effect of increasing the wax content on the damping factor versus the temperature of the urea-EVA moulding compounds**

Increasing the temperature, the polymer (PVOH) content or the wax content results in a reduction in the storage modulus (Figures 73 and 74). This implies that solid urea is stiffer than plasticised PVOH or wax. The loss modulus ( $E''$ ) shows the energy lost as heat is evolved.

The damping factor ( $\tan \delta$ ) is defined as:

$$\tan \delta = \frac{E''}{E'} \quad (46)$$

Where  $E''$  is the loss modulus and  $E'$  is the elastic modulus

A higher value of  $\tan (\delta)$  implies that the material has liquid-like rather than elastic solid properties. Figures 75 to 76 show strong  $\tan (\delta)$  peaks between 100 and 110°C. The peaks probably indicate that the amorphous PVOH-glycerol-urea phase of the material has become highly fluid.

The storage modulus versus temperature for the urea-EVA moulding compounds is shown in Figures 77 and 78. The storage modulus decreased systematically with an increase in temperature, wax content or EVA content. A step-wise drop is noted at temperatures above 50°C and is attributed to the melting of the semi-crystalline wax-EVA phase of the material. The steep drop in the storage modulus above 100 °C is due to the melting of the urea phase.

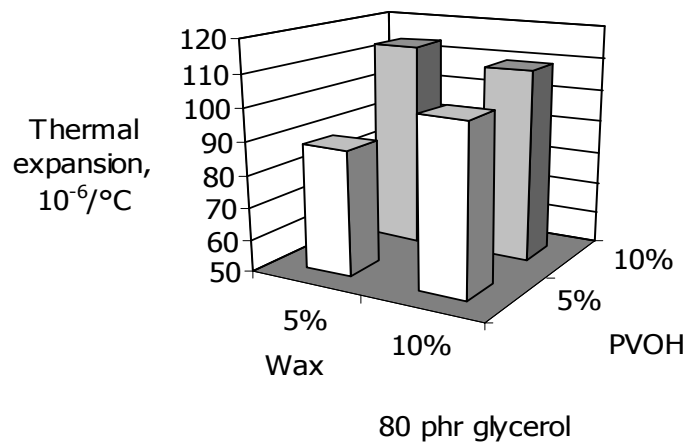
Figures 79 and 80 show a weak  $\tan (\delta)$  peak between -10°C and 30°C, and strong  $\tan (\delta)$  peaks between 55°C and 65°C and between 125°C and 130°C. The first and second peaks correspond to the glass transition temperature ( $T_g$ ) and the melting of the EVA/wax phase, while the highest temperature peak indicates melting of the urea phase. The peaks of the EVA/wax blend increase with an increase in the EVA or wax content. This confirms that the EVA/wax blend is a separate phase in the compound. The DMA results are consistent with the DSC observations with respect to the phase-separated nature of the compounds.

To conclude, the DMA results are consistent with the behaviour of phase-separated compounds in which the urea crystals act as reinforcing filler and the polymers and wax act as binder. Thus the stiffness relates directly to the urea content. That is why the PVOH-based compounds are stiffer than the EVA-based moulding compounds. The variation in the DMA storage modulus with

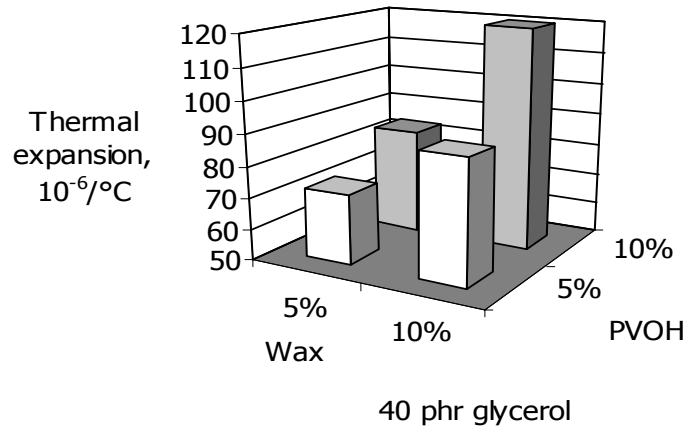
composition is consistent with the corresponding results obtained for the modulus of elasticity in the three-point bending tests.

### 8.5 Thermal expansion properties

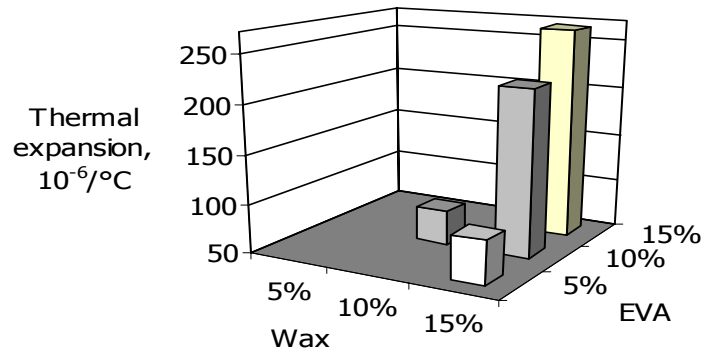
Investment casting pattern materials such as wax expand and contract with changes in temperature. The extent of thermal expansion of the material is crucial as it determines the pressure that will be generated in the green ceramic shell when the moulding compound is removed by a heat treatment. Shrinkage occurs which also affects the dimensional stability of a wax pattern. Fillers are added to wax mainly to reduce the thermal expansion coefficient and reduce expansion during heating.



**Figure 81: Thermal expansion coefficients measured at various temperatures for the PVOH (80 phr glycerol) compounds measured at 30°C - 40°C**



**Figure 82:** Thermal expansion coefficients measured in the temperature range 30 - 40 °C for the PVOH (40 phr glycerol) compounds



**Figure 83:** Thermal expansion coefficients measured in the temperature range 30 - 40 °C for the EVA moulding compounds

Figures 81, 82 and 83 show that as the polymer or the wax contents are increased, the linear thermal expansion coefficient increases. This is because the polymeric phases have a much higher thermal expansion than urea.

Similar results from the effect of increasing the wax or polymer contents were shown by the EVA moulding compounds this is shown in Figure 83. However, the PVOH moulding compounds have superior thermal expansion coefficients because there are more highly filled with urea than the EVA moulding compound.

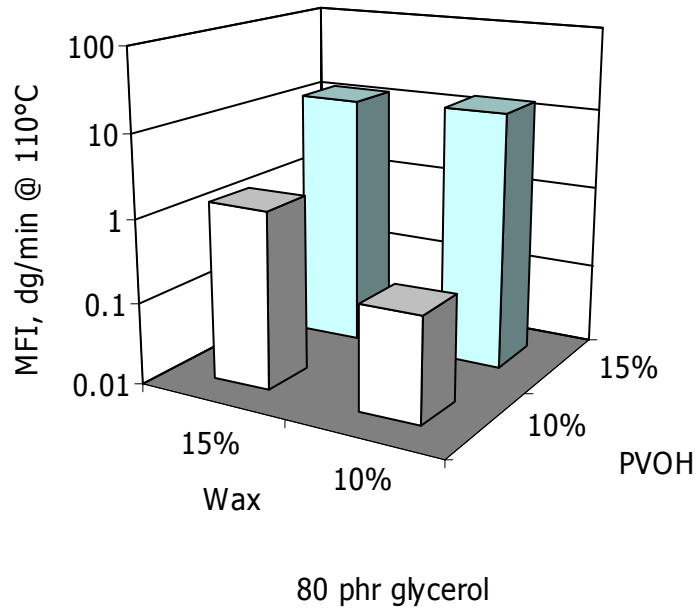
## **8.6 Melt flow index**

The melt flow index (MFI) quantifies the ease of flow of a polymer. It is defined as the weight of polymer in grams flowing in 10 minutes (g/10min) through a capillary of a specific diameter. Polymer systems with high MFIs are easier to process during the extrusion, injection moulding and de-waxing processes. It proved impossible to obtain reliable MFI data with the urea-wax-PVOH compounds containing less than 10% polymer or wax. This is attributed to gross phase separation taking place during the heating stage and to the urea degrading when heated at 110°C for 5 to 10 minutes. Relevant data could only be obtained at levels of 10% polymer and wax or more. The urea-wax-EVA moulding compounds did not show this behaviour.

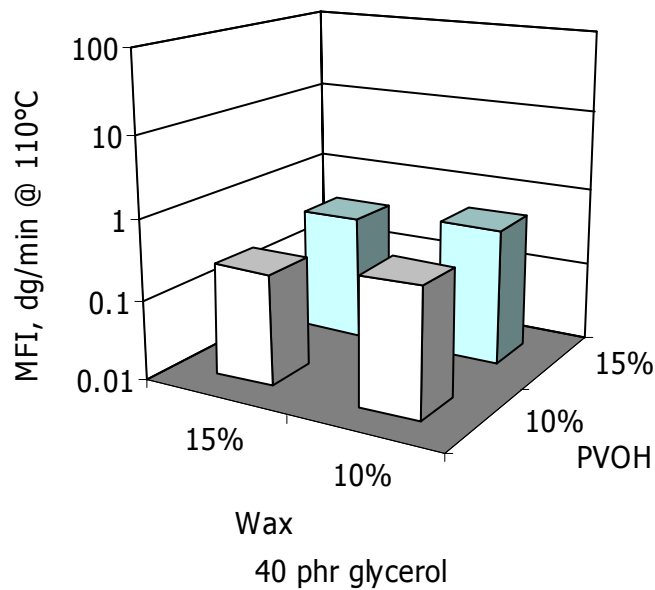
Figure 84 shows that the MFI increases with an increase in the polymer content, as expected. The blend MFI decreases because urea acts as filler, increasing the viscosity and reducing the ease of flow.

As the wax content is increased, the MFI increases when the PVOH content is 10%. However, at 15% PVOH, additional wax showed little effect: the wax may be acting as an external lubricant but the glycerol plasticiser could have a similar action.

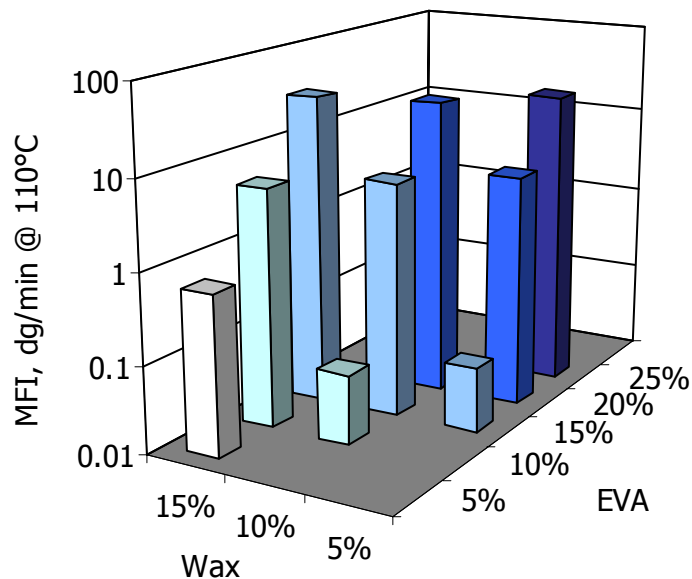
Figure 85 shows that a decrease in the degree of plasticisation from 80 to 40 phr reduces the MFI. Adding more plasticiser would increase the MFI of the base polymer but could also increase the MFI via an external lubrication effect.



**Figure 84: MFI of the urea-wax-PVOH (80 phr glycerol) compounds**



**Figure 85: MFI of the urea-wax-PVOH (40 phr glycerol) compounds**



**Figure 86: MFI of the urea-EVA-wax moulding compounds**

Figure 86 shows that an increase the wax or EVA contents causes the MFI to increase. This is because the wax acts as an internal lubricant and also because it forms compatible blends with EVA.

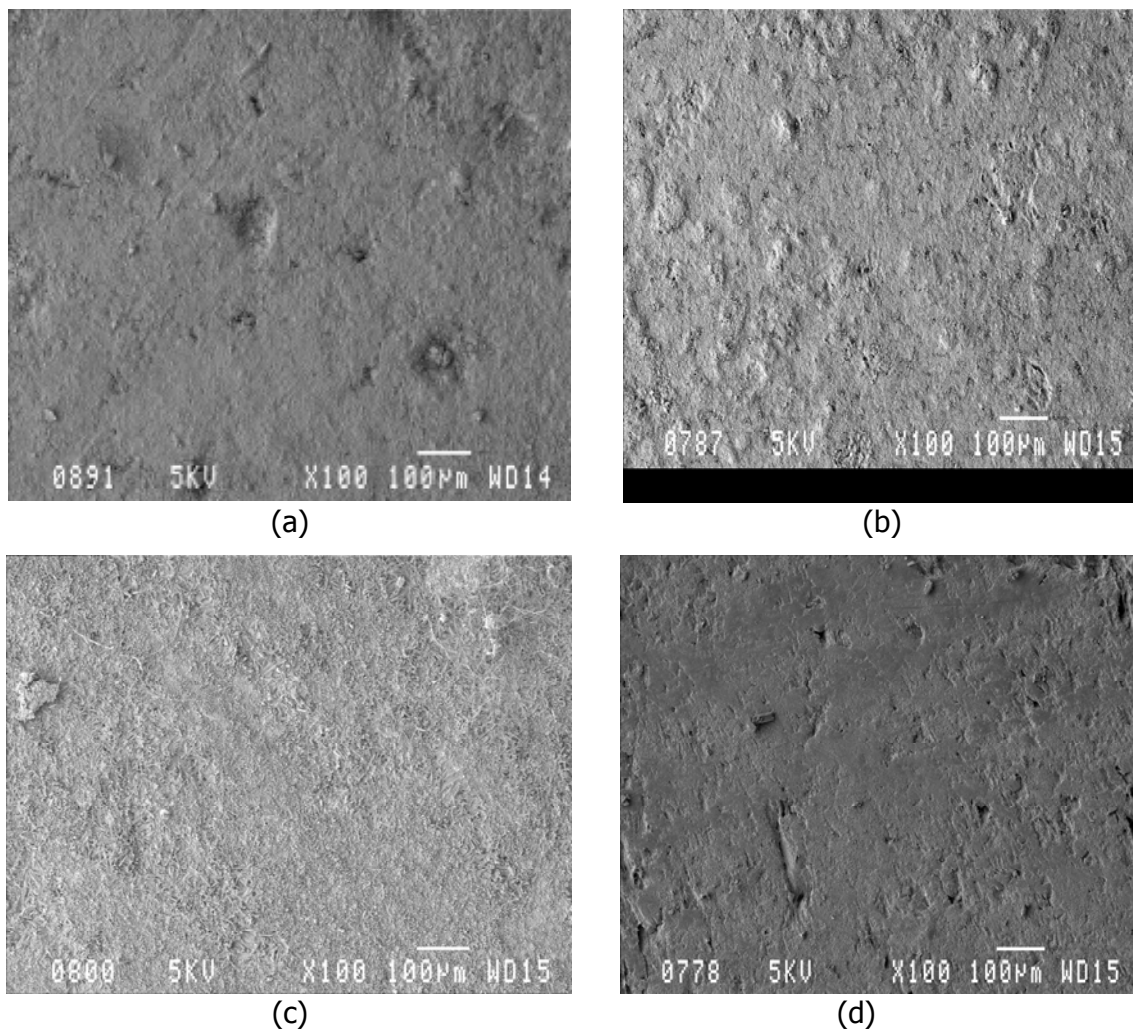
The MFI of the urea-EVA blend decreases as the urea content is increased. This is because, at the temperatures and pressures at which the measurements were taken, urea will be a solid particulate phase, i.e. it will act as filler. Fillers increase the viscosity of liquids. This explains the difficulties encountered when it was attempted to inject EVA moulding compounds containing 80% or more of urea.

The cooked urea-based moulding compound had better flow properties than any of the PVOH or EVA moulding compounds prepared in this study. Its MFI was 45.58 dg/min at 110°C as indicated in Appendix E.

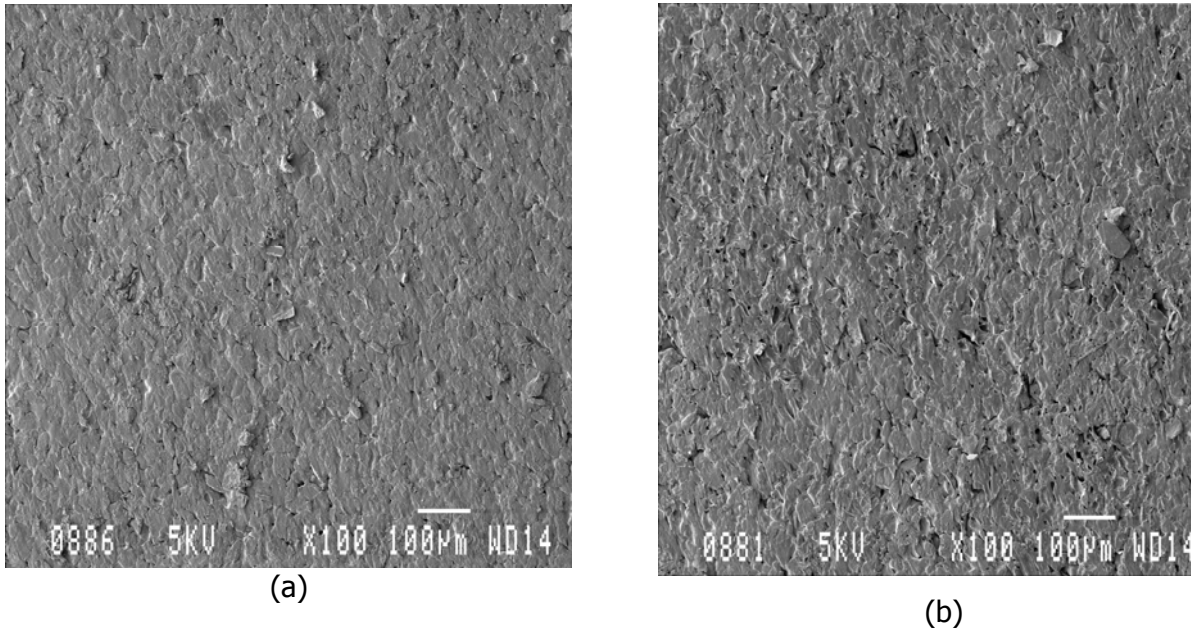


## 8.7 Scanning electron microscopy

A rough surface on a pattern will give a rough surface on the ceramic mould which, in turn, will result in a rough-surfaced finished metal part. This metal part will then require machining following the investment casting stage. This adds unnecessarily to the manufacturing cost and must therefore be avoided. This study used scanning electron microscopy (SEM) to investigate (superficially) the surface of injection-moulded samples of the moulding compounds. The effect of composition on the surface texture was studied using a qualitative assessment.



**Figure 87: SEM photographs of the surfaces of specimens of the PVOH urea-based moulding compounds: (a) UP8 90:5:5, (b) UP8 85:5:10, (c) UP8 80:5:15 and (d) cooked urea (benchmark)**



**Figure 88: SEM photographs of the surfaces of specimens of the EVA-urea-based moulding compounds: (a) UE 70:20:10 and (b) UE 80:10:10**

Figures 87 and 88 show the surface appearance of injection-moulded specimens used in the tensile strength tests. All the photos show surface inhomogeneities. Increasing the wax content appears to cause an increase in the surface roughness (Figure 87) of the PVOH urea-based compounds. The cooked urea-based moulding compound (benchmark) and the two-roll milled PVOH urea-based moulding compound have similar surface appearances.

Figure 8 shows that a slightly smoother surface is obtained when the EVA content is increased. It is evident that the PVOH moulding compound has a smoother surface texture than the EVA compound. The SEM photos also suggest that the reason might be poorer adhesion between the phases in the EVA-based compound. This is because EVA which is hydrophobic has weak interaction with the urea which is hydrophilic.

## 8.8 Density

The density of the compound is an important aspect in relation to the mixing of pattern during wax injection. Tables 31 and 332 list the densities of the current formulations. The densities of the raw materials are given in Table 31. The density of cooked urea moulding compound was 1,120 g/cm<sup>3</sup>.

**Table 31: Theoretical and measured densities of the EVA-urea-based compounds**

	Measured density (g/cm <sup>3</sup> )	Theoretical density (g/cm <sup>3</sup> )
UE 80:15:5	1,137	1,210
UE 80:10:10	1,168	1,192
UE 80:5:15	1,139	1,174
UE 75:10:15	1,145	1,151
UE 70:15:15	1,121	1,136

**Table 32: Theoretical and measured densities of the PVOH urea-based compounds**

	Measured density (g/cm <sup>3</sup> )	Theoretical density (g/cm <sup>3</sup> )
UP8 90:5:5	1,280	1,274
UP8 85:10:5	1,256	1,271
UP8 80:15:5	1,259	1,268
UP8 80:10:10	1,2253	1,228
UP8 80:5:15	1,2332	1,192

**Table 33: Density of the raw materials**

	Measured density (g/cm <sup>3</sup> )
Urea	1,32
Glycerol	1,26
PVOH	0,64
EVA	0,95
Paraffin wax	0,75

As shown in Tables 29 and 30, the density increased as the urea contents increased but were slightly lower than the theoretical density. The measured values were invariably lower, suggesting a degree of porosity in the samples.