

## CHAPTER 6 MATERIALS AND SAMPLE PREPARATION

### 6.1 Materials

Two different urea-polymer systems were investigated as potential compoundable moulding compounds:

- Ethylene vinyl acetate (EVA)
- Glycerine plasticised PVOH.

In each case paraffin wax was used as lubricant. The raw materials used are described in Table 9.

**Table 9: Virgin polymers and their suppliers**

Item	Grade	Density kg/m <sup>3</sup>	Description	Supplier
Urea	Fertiliser grade	1 340	Melting point: 133°C Decomposition temperature: 133°C pH: 7.1 - 8.4	Algro Brits
PVOH	Celvol 504	640	Melting temperature: 133°C Degree of hydrolysis (%): 87 - 89 Viscosity 4% solution@ 23°C: 55-70 cps pH: 4.5 - 6.5	Celanese
EVA	Elvax 210	951	Vinyl acetate content (wt %): 28 MFI: 400 dg/min @ 190 °C/2,16 kg Tensile strength: 2.8 MPa Elongation at break (%): 800 - 1,000	DuPont
Wax	M3X		Melting point: 60 - 65°C Penetration (0.1 mm): 17 - 24 Oil content (%): 2.4 - 3.4	Sasol Schumann
Glycerol	CP grade	1 260	Boiling point: 290°C Melting point: 18°C	Promark Chemicals

The formulated compositions were compounded using a conventional extrusion process and a two-roll mill. Both the patterns were injection moulded.

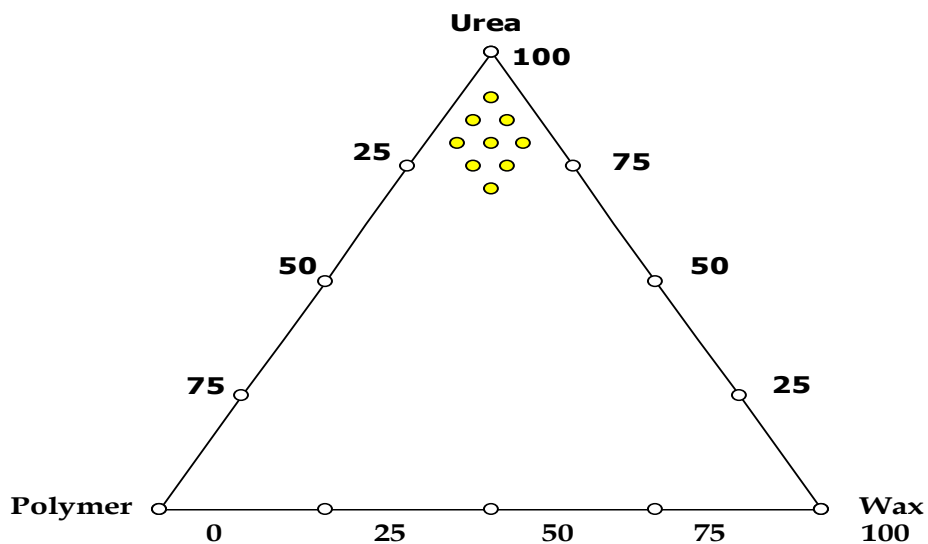
Both the patterns were characterised using the same approach to meet the requirements for investment casting. The characterisation techniques are fully explained in Chapter 7. The experimental design and sample preparation methods used to produce the PVOH, EVA and cooked urea-based moulding compounds are fully explained in this chapter.

Finally, the results obtained from characterisation techniques were compared with the industrial cooked urea-based pattern to see if the moulding compound would meet the specified requirements. The method of preparing and compositions of cooked urea based moulding compounds is shown in Appendix D.

## **6.2 PVOH urea-based moulding compounds**

### ***6.2.1 Experimental design***

A ternary system using urea, plasticised PVOH and wax was designed to formulate the composition necessary for exploration. The formulations explored in the ternary system are depicted in Figure 25. All compositions are on a mass basis unless otherwise indicated. The exception is the plasticiser content of the PVOH, where the technical usage of phr (parts per hundred of resin) was adopted. The formulations explored are further described in Table 10.



**Figure 25:** The ternary phase diagram showing compositions explored

**Table 10:** The compositions explored to make the PVOH urea-based compounds

Experiment	Urea (mass %)	Polymer (UP4) (mass %)	Wax (mass %)
A	90	5	5
B	85	10	5
C	80	15	5
D	85	5	10
E	80	10	10
F	75	15	10
G	80	5	15
H	75	10	15
I	70	15	15

**Note:** The experiments were repeated using UP8 (PVOH urea-based moulding compound of plasticisation degree 80)

### **6.2.2 Sample preparation**

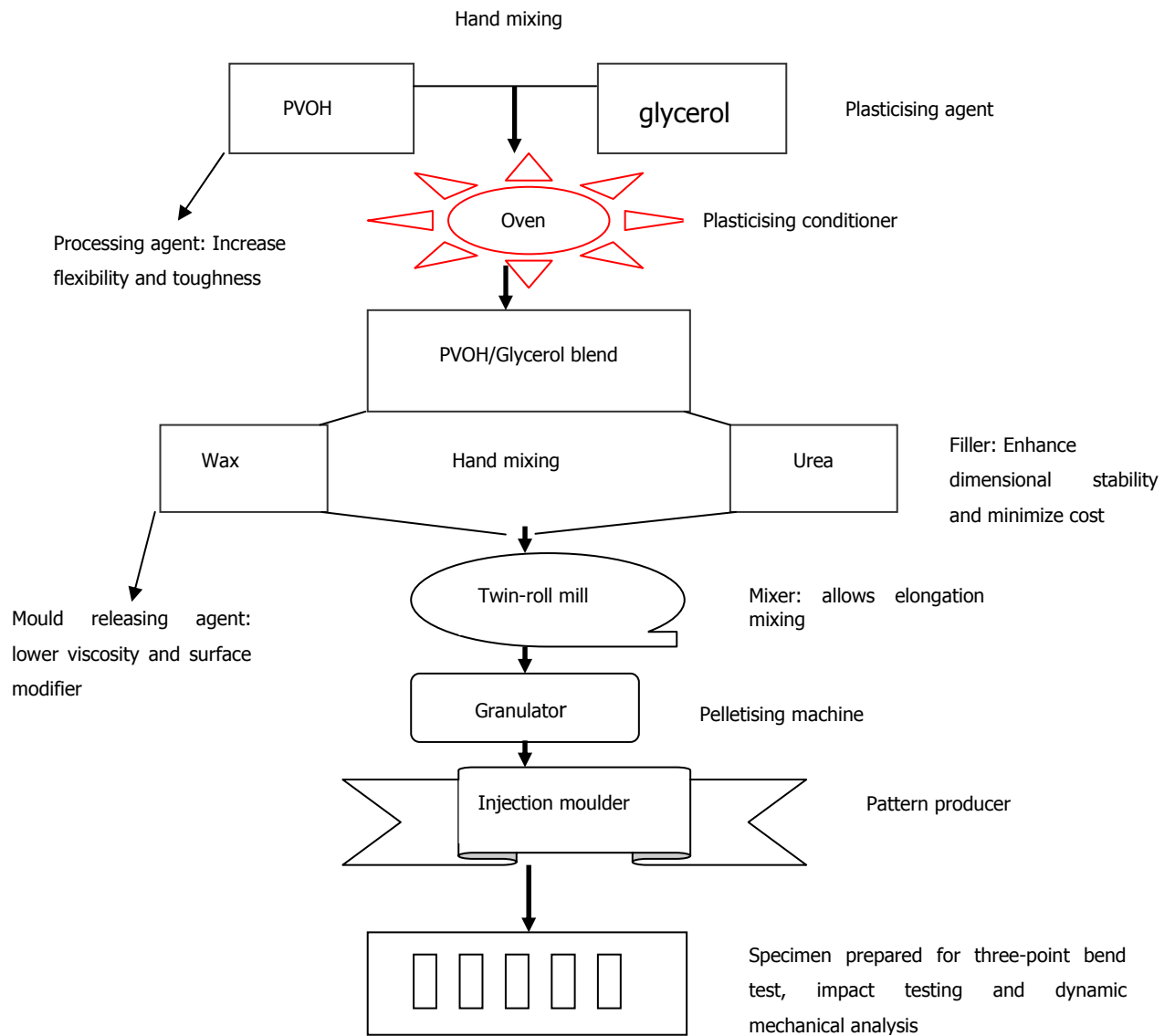
Figure 26 outlines the experimental procedure followed for the preparation of the biodegradable PVOH urea-based moulding compound. Urea prills were milled down to a particle size of ca. 150  $\mu$ m using a laboratory milling machine (Polymer Chip Grinder, Engineering Works). PVA was impregnated with glycerine as follows:

- The PVOH powder was hand-mixed with the glycerol using a stirring rod.
- The mixture was then conditioned in a laboratory oven at 80°C for 8 h.
- These PVOH/glycerol blends were then compounded in a laboratory two-roll mill set at a temperature of 110°C.
- Once the PVOH mixture had fluxed, the mixture of urea and wax powders was added portion-wise and mixed in.

The operating conditions are detailed in Table C2 in Appendix C. Mixing was terminated once a homogeneous blend had been obtained, as judged by the human eye.

The adjustable nip between the two counter-rotating speed rolls was then set at a 5 mm gap and the product rolled into a sheet form. The sheets were pelletised using a granulator. These were then injection-moulded on an Engel 3040 machine with an 800 kN force. Typical barrel temperatures, from the feeding zone to the nozzle, were varied between 100 -110°C. The injection-moulding parameters had to be optimised for each sample as the fluidity and processability varied significantly between the different formulations. Typical process conditions are given in Table C3 in Appendix C.

At least 12 test specimens were moulded for each formulation. The moulded tensile specimens had dimensions of 4.0 x 10.0 x 80 mm. These samples were used for three-point bending testing, Charpy impact testing and dynamic mechanical analysis.



**Figure 26: Outline of the preparation procedure used to produce the PVOH Urea-based compounds**

### 6.3 EVA urea-based moulding compounds

#### 6.3.1 Experimental design

A ternary system was designed to formulate the compositions necessary for exploration. The formulations explored are tabulated in Table 11.

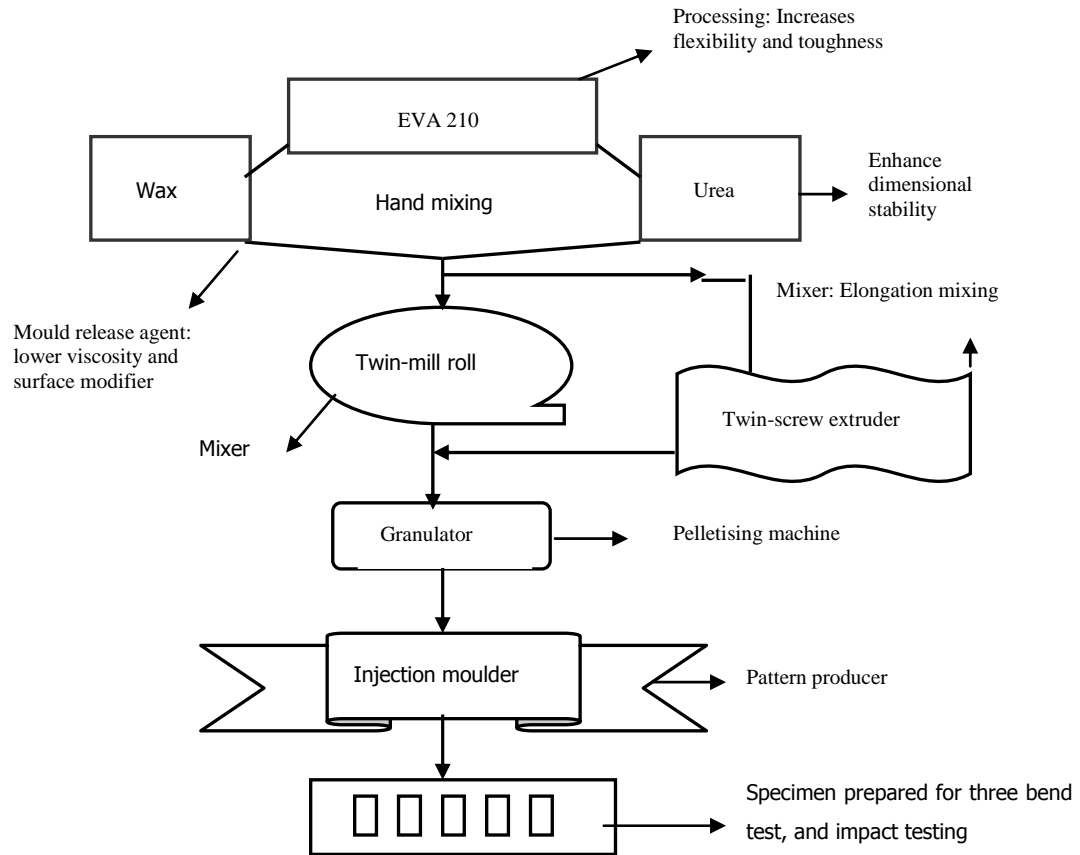
**Table 11: Compositions explored for the synthesis of EVA urea-based compounds**

<b>Experiment</b>	<b>Urea (mass %)</b>	<b>EVA (mass %)</b>	<b>Wax (mass %)</b>
A	80	15	5
B	80	10	10
C	80	5	15
D	75	20	5
E	75	15	10
F	75	10	15
G	70	25	5
H	70	20	10
I	70	10	15
J	65	20	15

### ***6.3.2 Sample preparation***

For the development of a urea-based pattern, urea prills were milled to a size of 150  $\mu$  m using a laboratory milling machine.

The compounding of urea/EVA/wax/blends was done on a Berstorff co-rotating twin-screw extruder. The operating conditions are specified in Table C1 in Appendix C. The strands were pelletized to produce pellets for injection moulding using a granulator. Six pieces of each composition were made under the processing conditions given in Table C3 in Appendix C. Moulds for tensile strength testing were made with the following dimensions: 4 mm x 10 mm x 80 mm. The samples were to be used for the three-point bending test, Charpy impact testing and dynamic mechanical analysis to characterise the mechanical and viscoelastic properties of the pattern. An outline of the preparation of the EVA urea-based compound is shown in Figure 27.



**Figure 27: Outline of the preparation procedure used to produce the EVA urea based compounds**

### ***6.3.3 Determination of the urea-acetamide phase diagram***

The phase diagram of the urea-acetamide system was determined using the cooling method as described by Walbrugh (2006). The results of these experiments are presented in Figure 3, Chapter 3. This work was done because it was initially believed that it would be necessary to use a urea eutectic to lower the possible processing temperature in order to avoid degradation of the urea during the compounding and shaping processes. It turned out that this was not necessary.

## **CHAPTER 7 CHARACTERISATION OF THE COMPOUNDS**

Filled investment casting patterns form complex blends, which contain the following ingredients: fillers, resins and paraffin wax. These ingredients are used to develop the desired pattern to meet the specific requirements of an investment caster. Both compounds were analysed and the results were compared with the industrial cooked urea-based pattern using the characterisation techniques described below.

### **7.1 Mechanical properties**

#### ***7.1.1 Three-point bending test***

The three-point bending test was performed to determine the mechanical properties of the urea-based compounds. Six samples of dimensions 4 mm x 10 mm x 80 mm of each type of formulation prepared were tested in accordance with ASTM Standard D790. The samples were stored under ambient conditions for 24 h. Lloyd Instruments Instron Series IX for automated material testing, of capacity 5 kN, was used to apply the load over a 64 mm span, linked to a PC. All tests were performed using a cross-head speed of 1.8 mm/min. The value of "maximum load, maximum deflection" was used to calculate the Young's modulus of bending and the modulus of rupture. The results of the tests were processed using the equations given in Chapter 5.

#### ***7.1.2 Impact strength***

Charpy impact tests were employed to obtain a qualitative indication of the material toughness. Charpy impact resistance was determined using a pendulum machine (Zwick) with a weighing capacity varying from 10 - 40 kp.cm. Ten unnotched specimens of dimensions 50 mm x 10 mm x 4 mm (length x width x thickness) were cut and machined from injection moulded tensile testing specimen.



## **7.2 Dynamic mechanical analysis**

The injection-moulded patterns were cut and machined into rectangular bars of dimensions 10 mm x 10 mm x 4 mm (length x width x thickness). Dynamic mechanical analysis (DMA) was done on an instrument (Perkin-Elmer DMA 7e) at temperatures ranging from -50 to 150°C at 10 Hz.

## **7.3 Thermomechanical analysis**

The injection-moulded patterns were cut and machined into rectangular bars similar to those prepared for DMA. Thermomechanical analysis (TMA) was done using the Vicat softening point which defines the softening temperature as the point at which the probe penetrates by 1 mm. TMA analysis was done at temperatures ranging from 25 to 150°C, at a heating rate of 5°C per minute using a static force of 1N and a probe with a diameter of 1 mm.

## **7.4 Thermal properties**

### ***7.4.1 Differential thermal analysis and thermogravimetric analysis***

A small amount of sample (10 - 15 mg) was used. The tests were conducted in liquid nitrogen and the samples were heated from 25 to 800°C at a heating of 10°C per minute.

### ***7.4.2 Differential scanning calorimetry***

Thermal analysis was performed from 30 to 140°C at a heating rate of 5°C/min under liquid nitrogen using a differential scanning calorimeter (DSC) (Perkin-Elmer 7). The temperature was maintained for 1 minute and was then decreased to room temperature at a cooling rate of 5°C per minute.

## **7.5 Melt flow index**

Melt flow index (MFI) measurements of the urea-based patterns were obtained in accordance with ASTM Standard D1238 (Procedure A) at 110°C using a 2,16 kg load. The MFI apparatus was purged before the next sample was tested to ensure accuracy.

## **7.6 Scanning electron microscopy**

The surface morphology of the investment casting patterns was studied using a JEOL scanning electron microscope (SEM) at 10 kV. The surfaces of the patterns were coated with gold for photographic purposes.

## **7.7 Density**

Actual density was measured using the Archimedean Principle. (This principle states that a solid body immersed in a liquid loses as much of its own weight as the weight of the liquid it has displaced.) The sample was first weighed dry in air and then weighed while immersed in water and ethanol in the case of both the EVA urea-based compound and the PVOH urea-based compound. This was done using a pycnometer. The way the measurement and calculation was done is fully shown in Appendix H.