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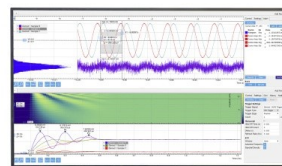
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# Thermal and mechanical properties of investment casting pattern material based on paraffin wax fortified with LLDPE and filled with PMMA

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**Abstract.** The thermal and mechanical properties of paraffin wax, linear low-density polyethylene (LLDPE) and poly (methyl methacrylate) (PMMA) microbeads formulations were prepared via extrusion process. The blends were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and its tensile properties (stress at break, strain at break and modulus of elasticity and). The results indicated that both LLDPE and PMMA had an influence on the thermal properties and the tensile properties of the blends. The TGA analysis showed that the thermal stabilities of the developed polymer increased and also at temperatures above 600 °C, there was no residue. DSC curves of the blends indicated two main exothermic peaks at 60 °C and 120 °C. This could be probably due to the wax structure and the LLDPE peak structure. DSC curves further suggested that the compatibility of the paraffin wax/LLDPE two phases increased with an increase in the filler content. The bending stress at break and the Young's modulus increased with increasing LLDPE content whereas the PMMA beads increased modulus there was no gradual strain increment.

## INTRODUCTION

For the past few decades, the use of polymer blends for many industrial applications such as pattern material for investment casting has been popular <sup>1</sup>. In the investment casting industries, modification of wax properties has been done by blending wax with other materials such as polymers, fillers and resins in order to develop a wax pattern which can have the functional properties for complex patterns <sup>2,3</sup>. Polymer blending depends largely on the miscibility or immiscibility of the components used. Immiscibility of polymers keep the good features of each of the base polymer components of the blend <sup>7</sup>. An example of the feature improved by immiscible polymers is the impact test.

Polyolefins are generally characterized by good processability, high flexibility, dimensional stability and excellent resistance to acids, bases and alcohols <sup>4,5</sup>. Linear low-density polyethylene is characterized by low-temperature properties which is a crucial functional property in investment casting process, heat tolerance and better tensile strength as compared to low density polyethylene (LDPE) <sup>4,6</sup>. Paraffin waxes (Fischer–Tropsch synthesis) aliphatic hydrocarbons are characterized by straight or branched carbon chains <sup>7,8</sup>. Some of the properties associated with paraffin wax include: (a) smooth texture; (b) water repellency; (d) good dielectric properties and (e) low toxicity levels <sup>9</sup>.

Blending paraffin wax with polyethylene such as LLDPE produces a polymer blend with valuable properties such as good processability, low cost and light weight which gives the right compromise of the properties of the finished

products<sup>6</sup>. Several researchers have conducted lots of studies on the preparation of paraffin wax and polyethylene-based polymer blends via extrusion, injection molding, mechanical mixing and melt-mixing methods. Krupa & Luyt (2001b)<sup>10</sup> studied on the physical properties of blending LLDPE with oxidized wax affects. The authors concluded that the stability of wax is improved by blending with LLDPE. Hato & Luyt (2006)<sup>11</sup> researched on blending different types of polyethylene's and waxes together. Mhike et al. (2012)<sup>12</sup> investigated on melt blending of wax, LDPE and graphite to develop a phase change material. Chen & Wolcott (2013)<sup>5</sup> researched on crystallization and co-crystallization behavior of polyethylene and paraffin wax blends.

The present study explores the utilization of a paraffin wax modified with linear low-density polyethylene and filled with poly (methyl methacrylate) (PMMA) as polymer-based blend for investment casting process pattern. Paraffin wax, LLDPE and PMMA was developed by extrusion process. The produced blend was characterized in terms of its thermal properties and mechanical properties.

## MATERIALS AND METHODS

### Materials

Paraffin wax (M3B) (Congealing point = 62 °C, mean molecular mass = 785 g.mol<sup>-1</sup>, density 0.900 g.cm<sup>-3</sup> at 25 °C) was obtained from Sasol Performance Chemicals. LLDPE (melting point = 70 °C, density 0.926 g.cm<sup>-3</sup> at 25 °C and melt flow index (MFI) 50 g/10 min@190 °C, 2.16 kg) was supplied by Sabric, SA Pty. Advanced Polymers supplied PMMA microbeads. All the materials were used as received.

### Method

The experimental design used for the wax/LLDPE/PMMA formulations followed Fig. 1. The formulations were compounded using a TX28P 28 mm co-rotating twin-screw extruder with an L/D ratio of 18. The temperature profile used for processing of the wax/LLDPE/PMMA formulations from hopper to die was 65/120/150/160 °C. The melt was extruded directly into a water bath.

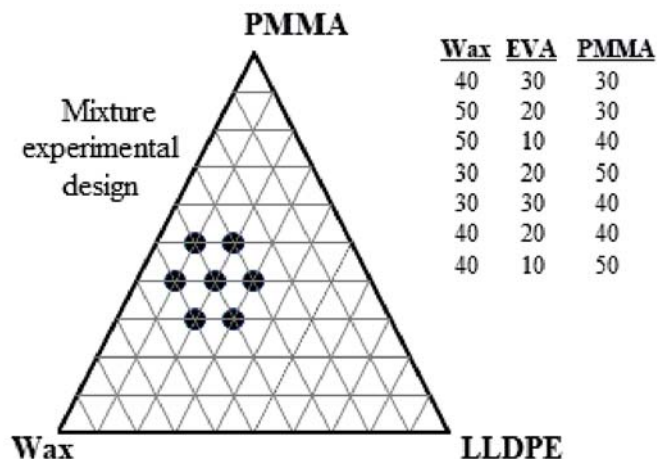


FIGURE 1. Experimental design for the wax/EVA/PMMA blend formulations

## Characterization Techniques

### Thermal studies

Thermal behaviour was done by TGA and DSC using a TA Instruments SDT Q 600 TGA and a Perkin Elmer DSC 4000 analyzer respectively.  $8 \pm 2$  mg were placed in a 70  $\mu$ L alumina pan and scanned from 25 to 900 °C at a scan rate of 10 K.min<sup>-1</sup> for TGA. In the case of DSC sample masses weighing  $15 \pm 2$  mg were placed in sealed aluminium pans and heated at 20 K.min<sup>-1</sup> from at 20 °C and 200 °C.

### Thermomechanical analysis (TMA)

Needle penetration tests were conducted to determine the hardness of wax/LLDPE/PMMA formulations<sup>13</sup>. The penetration measurements were conducted at 30 °C on a TA Instruments Q400 Thermo Mechanical Analyzer fitted

with a needle with a tip radius of 1.4 mm. A wax/LLDPE/PMMA sample was cast in a 90  $\mu\text{L}$  alumina pan. The applied force was set at 0.001 N and was increased after two-minute intervals using the following successive force increments: 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 N and 1 N. During the experiment, the penetration depth of the needle was tracked as a function of time.

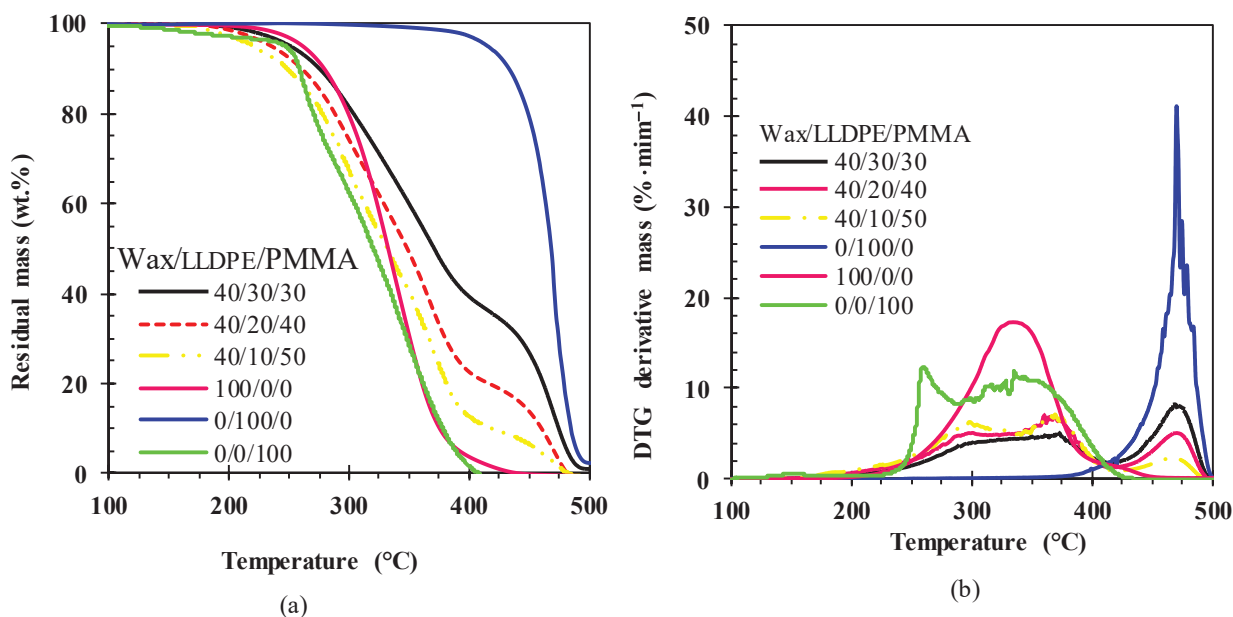
### Three-point bending tests

The mechanical properties of the extruded wax/LLDPE/PMMA blends were conducted via three-point flexural testing, executed according to ASTM 790. The testing was performed on an Instron 5564 twin column tensile tester fitted with a 5 kN load cell at room temperature. The mould used for the specimen preparation was also fabricated using silicon. Test bars for three-point bending (10 x 10 x 80 mm) were cast from the melt using a silicone rubber. The crosshead speed was set at 1.8  $\text{mm}\cdot\text{min}^{-1}$  and the sample support span was 64 mm. An average of five specimens were taken in reporting the yield stress and strain at break.

## RESULTS AND DISCUSSION

### Thermogravimetric Analysis (TGA)

Fig. 2 (a) and (b) shows the TGA and DTG curves of wax, LLDPE, PMMA and wax/LLDPE/PMMA blends respectively. As it can be seen in Fig. 2 (a), LLDPE is more thermally stable than both wax and PMMA and its degradation occurred in one step at a temperature of about 360  $^{\circ}\text{C}$  to 530  $^{\circ}\text{C}$ . This can be attributed to the decomposition of C-C bonds present in the main LLDPE chain. Wax has two distinct degradation peaks at around 210  $^{\circ}\text{C}$  and 396  $^{\circ}\text{C}$  associated with concurrent evaporation and thermal degradation events. The DTG curve as shown in Fig. 2 (b) for the wax suggests that the apparent mass loss occurred, for the most part, as a one-step process. The second degradation peak at around 230 – 300  $^{\circ}\text{C}$  can be attributed to degradation of unsaturated chains of PMMA and the third degradation peak at around 320  $^{\circ}\text{C}$  can be related to random scission of polymer chains <sup>14</sup>.



**FIGURE 2.** (a) TGA curve and (b) DTG curve for the wax, LLDPE, PMMA and 40/20/40, 40/30/30 and 40/10/50 wax/ EVA/ PMMA blend.

### Differential Scanning Calorimetry (DSC)

Figure 3 (a) and (b) shows the DSC curves of wax, LLDPE and wax/LLDPE/PMMA during heating and cooling respectively. As it can be seen in Fig.3 (a), wax has a sharp distinct main peak at a temperature of 60  $^{\circ}\text{C}$  which represents the solid-liquid phase change of the wax. The minor peak at a temperature of 38  $^{\circ}\text{C}$  corresponds to the solid-solid phase transition of wax. <sup>12,15</sup> reported similar peaks match of pure paraffin wax. LLDPE has one endothermic at a temperature around 125  $^{\circ}\text{C}$  as it can be seen in Figure 3 (a). This can be associated with the melting

of the LLDPE matrix. During cooling as shown in Fig. 3 (b), LLDPE has a main exothermic peak at around 105 °C. This peak corresponds to the crystallization of LLDPE chains.

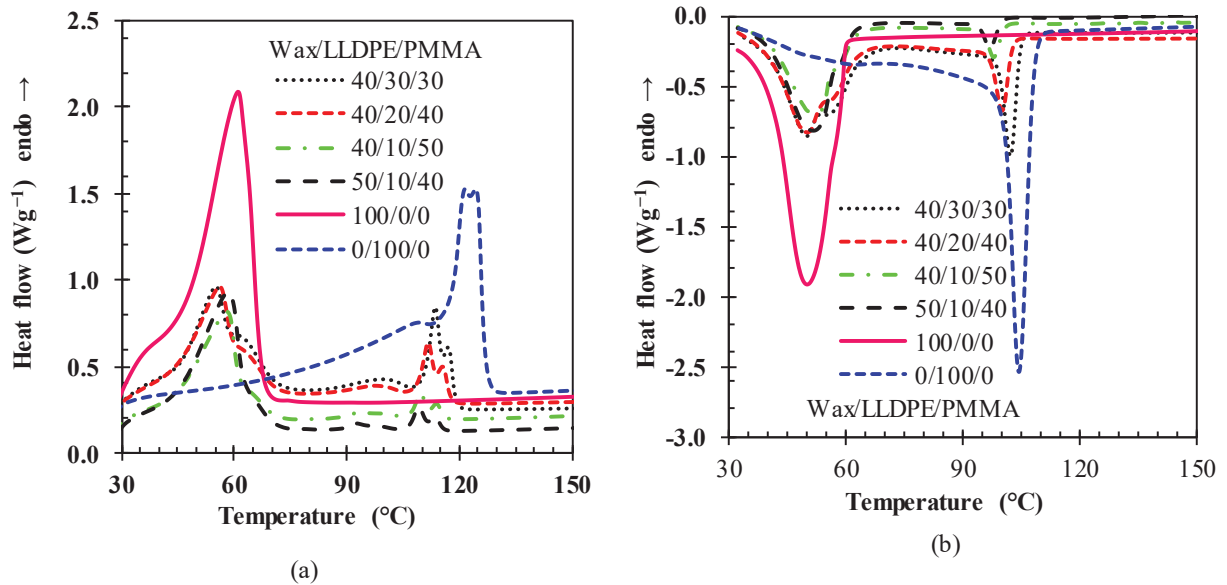


FIGURE 3. (a) DSC heating and (b) DSC cooling curves obtained for the wax, EVA, PMMA and the 50/10/40 wax/ EVA/ PMMA blend.

### Three-point Bending Tests and Penetration Tests via TMA

Tab. 2 represent the bending strength, the bending strain at break and the Young modulus of elasticity for wax, wax/LLDPE/PMMA blends. As it can be observed in Tab. 2, the bending strength increased with an increase in LLDPE amount, whereas the stain at break decreased in all the formulations except the formulations with a higher LLDPE content. Wax/LLDPE/PMMA blends containing the highest amount of LLDPE (30% -weight) failed in a ductile fashion when load was applied even failed in a ductile fashion. The bending strength properties are mainly depending on polymer crystallinity. Generally, interfacial adhesion between the polymer have a great influence on its mechanical properties. This can be attributed to the branched nature of LLDPE, which is characterized by a lower bonding forces between chains and lower degree of crystallinity. Studies by <sup>16</sup> indicated that fillers have an effect on the modulus of polymer blends due to polymer chain disruptions. The authors further concluded that the Young modulus is not affected by poor adhesion as in the case of tensile strength. Furthermore, as it can be seen in Tab. 2, the needle easily penetrated in neat wax but there was some resistance from the neat LLDPE. It can also be seen that when the force applied is increased, the needle penetration continues during the full 2 min testing interval but the rate of penetration decreases over time.

TABLE 1. Three-point bending results

Wax	LLDPE	PMMA	Stress (MPa)	Strain (%)	Modulus (MPa)	Penetration (µm)
100	0	0	1.3±0.1	1.7±0.5	38±20	327
30	20	50	5.0±0.3	1.3±0.2	676±61	122
30	30	40	7.8±0.7	2.2±0.4	671±74	29
40	10	50	2.8±0.3	1.0±0.2	417±80	83
40	20	40	4.8±0.4	1.3±0.2	708±197	45
40	30	30	6.2±0.2	1.8±0.1	607±70	50
50	10	40	3.2±0.4	0.8±0.1	541±101	84
50	20	30	3.8±0.8	1.3±0.2	515±121	44

\*Needle penetration test. Depth measured after application of a final force of 1 N for 2 min.

## CONCLUSION

In summary, the following conclusions were drawn:

1. LLDPE and PMMA incorporation into melt on wax has an influence in wax thermal properties. The TGA showed that thermal stability of paraffin wax was improved with blending with LLDPE and PMMA;
2. The DSC curves showed that multiple endothermic and exothermic peaks during heating and cooling obtained. The first distinct peak is associated with the Fischer–Tropsch paraffin wax solid-solid transition as well as its melting and the second distinct peak was due to LLDPE. At lower LLDPE content, miscibility of the blend can be possible;
3. Higher tensile strength and Young modulus was witnessed in the blends as compared to the neat paraffin wax. These are of great importance when determining the stiffness and allowable load in materials.

## ACKNOWLEDGMENTS

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