Production of Polyester Resin Reinforced Thermosetting Polymeric Material from A Stackable Thermoplastic (Polypropylene)

U. Ibeneme¹; P.A.P Mamza² & H. Abba²

¹Department of Polymer Technology,. Directorate of polymer and Environmental Technology, Nigerian Institute of Leather and Science Technology, Samaru, Zaria, Nigeria
ibenemeuche@rocketmail.com; 08023919795

²Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria
paulmamza@yahoo.com. 08037030398

²Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria
hamzaabbah@yahoo.com 08028333784

*Corresponding Author: U. Ibeneme ibenemeuche@rocketmail.com 08023919795

ABSTRACT
In this research, glassfibre reinforced polyester composites were fabricated. Unsaturated polyester resin was used as the polymer matrix and glassfibre was used as the reinforcing material. The main focus of this work was to fabricate a composite seat by the cheapest and easiest way. For this reason, hand layup method was used. The mould for the seat was fabricated with four layers of glassfibre (450g) weight. The mechanical properties of the various laminates (the control sample comprising 100% of the matrix) and the glassfibre with the matrix (laminates) were carried out. The tensile, flexural, and hardness test were done. From the experimental analysis of the tensile test, it was observed that the control sample had the least ultimate tensile strength/modulus of elasticity of 26.15Mpa and 93.39Mpa respectively. The tensile test/modulus of elasticity increased with the addition of glassfibre into the matrix. While the 6th laminates had the highest ultimate tensile strength/modulus of elasticity of 196.92Mpa and 729.33Mpa, The same trend happened in the flexural and hardness test. The control sample had a bending stress of 36.09Mpa and flexural modulus of 535.74Mpa while the 6th laminate had the highest bending stress of 300.76Mpa and flexural modulus of 8889.61Mpa. The hardness test increased gradually with the control sample having 86.66 shore and 6th laminate 96 shore. The morphology of the fillers dispersion into the matrix were observed using scanning electron microscopy at different magnifications. It was observed that Sem macrograph taken at higher magnification gave excellent bridging effect in the interfacial region of the glass fibre. The various laminates were immersed in water for 72 hours using a glass water beaker. It was observed that the 5th and 6th laminate absorbed only 3% and 1% of water respectively.

Keywords: Glassfibre, Matrix, Plastics, Crosslinking, Laminated Plastics.

INTRODUCTION
Glassfibre is made by rapidly drawing and cooling molten glass. Probably, the most familiar composite material today is glassfibre which is widely used to form large light weight reinforced structures, such as
the hull of a cabin cruiser or as alternatives to heavy porcelain in the manufacture of bathubs. Fibre glass, is the trade name for a composite consisting of glassfibre reinforcement of an unsaturated polyester matrix. Joel R, F, (2003).

There are two principal types of fibre glass. A coarse staple glassfibre is widely manufactured for use as thermal insulation. This is generally unsuitable for use as a plastic reinforcement. The other type consists of continuous filaments, which immediately after drawing are bundled together to form strands. These in turn are made into yarn for weaving into glass cloth, or into rovings. Glassfibre is one of the strongest of all materials. The ultimate tensile strength (UTS) of a freshly drawn single glass filament (diameter 9-15 microns) is about 3-5Gpa. It is non-combustible and chemically resistant. Scottbader, (1990). Glassfibre is therefore the ideal reinforcing material for plastics. As soon as resins were developed which could be cured without the application of pressure, Glassfibre was used successfully as reinforcement. This marked the origin of the glass reinforced industry. (GRP) The original plastic material without fibre reinforcements is known as the matrix. The matrix is a tough but relatively weak plastic that is reinforced by stronger stiffer reinforcing filaments or fibres.

The extent that strength and elasticity are enhanced in a fibre reinforced plastics depends on the mechanical properties of both the fibre and the matrix, their volume relative to one another and the fibre length and orientation within the matrix. Smallman, R, E, Bishop, R, J, (1999) Fibre reinforced plastics is composite material made of a polymer matrix reinforced with fibre. Glassfibre has many industrial applications, examples are aircraft, boats, automobiles, septic tanks, bathubs, water tanks, etc., Johnsoller, J, (2004) The development of fibre reinforced plastics for commercial use was being extensively researched in the 1930’s in the UK., Considerable research was being undertaken by pioneers such as Norman de brune. The research was particularly of interest to the aviation industry. In this research we have produced a fiberglass seat from a thermoplastic seat made of polypropylene polymer. Glassfibres are the most common fibres across all industries, although carbon fibres and carbon aramid fibres are found in aerospace and sporting applications. Erhand, G, (2006). Fibre reinforced plastics possess outstanding properties such as high strength to weight ratio and excellent corrosion resistance, easy fabricability are obtained by reinforcing a plastic matrix with a high fibre material. The high strength to weight ratio of fibre reinforced plastics makes it highly useful in aircrafts and satellites. Sharma, B, K, (2002)

**Polyester resin**

Unsaturated polyester resins are the condensation products of unsaturated acids or anhydride and diols with or without diacids. The unsaturation present in this type of polyesters provides a site for subsequent crosslinking. Arland, P, (1989). The polyester laminating resins are viscous, generally pale yellow coloured materials of low degree of polymerization(~8-10), i.e molecular weight of about 2000. A typical unsaturated polyester resin is that obtained from the polymerization of maleic anhydride and ethylene glycol

\[
\begin{align*}
Hc & \quad CH + H_2CH_2CH_2OH \\
OC & \quad O
\end{align*}
\]

\[
-\bigg\{H_2 CH_2OOC - CH = CH - OC \bigg\}_n
\]

**Figure 1: Polymerization Reaction of Maleic Anhydride and Ethylene Glycol**

Crystic resins are unsaturated polyester resin. This means that they are polyester resins capable of being cured from a liquid to a solid state. When subjected to the right conditions, They differ from saturated polyesters such as terylene which cannot be cured in this way. However, it is usual to refer to unsaturated resin as polyester resins. or simply polyesters. Most cystic resins are liquids. They consists of a solution of polyester in a monomer which is usually styrene. The styrene performs the vital function of enabling the
resin to cure from a liquid to a solid by crosslinking the molecular chains of the polyester without the evolution of any by-products. The resin can therefore be moulded without the use of pressure. They are contact or low pressure resins. The molecular chains of the polymers can be represented as follows;

Figure 2: Cross-linked Polymer

the addition of styrene ------S----- and in the presence of a catalyst and accelerator, the styrene Will crosslink the polymer chains to form a highly complex three-dimensional network as follows.

Figure 3: Representation of cross-linked polyester

The polyester resin is then said to cure. It is now a chemically resistant (and usually) hard solid. The crosslinking or curing process is called polymerization. It is a non-reversible chemical reaction. The unsaturation in the polyester is usually supplied by the inclusion of maleic anhydride as one component. In addition, a saturated acid or anhydride is often used, such as phthalic anhydride. A higher proportion of unsaturated acid gives a more reactive resin, with improved stiffness at high temperatures, while more of the saturated components give less exothermic cures and the less stiff resins. Billmeyer, J, R, Fred, W (1984)

Liquid polyester resins are unstable., After several months or years of storage they will set to a rubbery gel, even at normal room temperature this period is the storage life and shelf life of the resin and varies from one type of polyester to another. The storage life is considerably reduced at temperatures greater than 25°C. Most cystic resins have a storage life in the dark at 20°C. Of at least six months, and in some cases of at least more than one year. Pigmented cystic resins have a shelf life of three months. Soars, B, G, and, Burk, V, G (2008) They found that the gel time was reduced in case of functionalized polyesters, indicating an accelerating on curing process.

Laminated plastics are materials pressed from several layers of fibrous fillers impregnated or glued with a thermosetting resin. When pressing is done at elevated temperatures the resin gets hardened as a result of transfer into an infusible and insoluble state and forming a monolithic material with the filler. Laminated materials can be classified in a number of groups in accordance with the nature of the filler used. For example, cloth laminates (fabrics are the fillers) paper, laminates, and wood laminates (Sawdust or shavings are the fillers) Sharma, B, K (2011)

EXPERIMENTAL METHODS

The glassfibre, methyl ethyl Ketone peroxide (MEKP), black pigment and blue pigment, gelcoat, mirror glaze, mould releasing agent, cobalt accelerators, were all weighed with the electronic weighing balance. The mould pattern was taken from a thermoplastic seat as shown below;
The mirror glaze was used to clean the surface of the thermoplastic seat. A plastic bowl of 0.05kg was cleaned thoroughly with the mirror glaze using a cotton wool. The gel coat and the black pigment were measured and poured into the plastic bowl. 1% catalyst and 2% accelerator were added and the mixtures were stirred thoroughly using a stapler. The thoroughly mixed black gelcoat was then applied on the surface of the thermoplastic mould format using a lamination brush. The thickness of the gelcoat on the mould pattern was made even. A gelcoat of uneven thickness may cure at different times on the mould pattern. The mould pattern was touched with clean finger, the gelcoat was then at the right stage of lamination when the fingers came away perfectly clean from the mould pattern.

The glass fibre was cut to the size of the mould pattern and weighed. The weighed glass fibre, a liberal coat of polyester resin was mixed with catalyst and brushed over the gelcoat as evenly as possible and the first layer of glass fibre was pressed firmly into place and consolidated with a brush and rollers to remove air bubbles on the laminate. The glass fibre was chosen according to ASTM D578 standard specifications for glass fibre strands.

This process was repeated for the second, third and fourth layers and then reinforced with wood and then allowed 72 hours to cure completely. The mould was released, cleaned and waxed thoroughly, the thermosets plastics seat was then produced from the casted mould using the same lamination process. The only difference was that the gelcoat used was blue gelcoat. The basic curing formulations table is shown below:

![Figure 4: Cast thermoset seat from the fabricated mould](image)

**Table 1: Resin Fibre Formulations for the Various Laminates**

<table>
<thead>
<tr>
<th>S/N</th>
<th>Sample</th>
<th>Mass of Resin (g)</th>
<th>Mass of Glass fibre (g)</th>
<th>Mass of Catalyst (g)</th>
<th>Mass of Accelerator (g)</th>
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<tbody>
<tr>
<td>1</td>
<td>control</td>
<td>50.00</td>
<td>0</td>
<td>5.00</td>
<td>5.00</td>
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<tr>
<td>2</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Laminate</td>
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<td>31.27</td>
<td>5.00</td>
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<td>3</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Laminate</td>
<td>72.96</td>
<td>33.27</td>
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<td>5.00</td>
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<tr>
<td>4</td>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Laminate</td>
<td>76.48</td>
<td>38.25</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
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<td>4&lt;sup&gt;th&lt;/sup&gt; Laminate</td>
<td>91.84</td>
<td>45.92</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>6</td>
<td>5&lt;sup&gt;th&lt;/sup&gt; Laminate</td>
<td>103.36</td>
<td>46.98</td>
<td>5.00</td>
<td>5.00</td>
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<tr>
<td>7</td>
<td>6&lt;sup&gt;th&lt;/sup&gt; Laminate</td>
<td>154.56</td>
<td>51.00</td>
<td>5.00</td>
<td>5.00</td>
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Table 2: Resin/Fibre Formulations for the Casting of Thermosetting Mould

<table>
<thead>
<tr>
<th>S/N</th>
<th>Laminate</th>
<th>Mass of Resin (g)</th>
<th>Mass of Fibre (g)</th>
<th>Mass of Gelcoat (g)</th>
<th>Mass of Black Pigment (g)</th>
<th>Mass of Catalyst (g)</th>
<th>Mass of Accelerator (g)</th>
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<tr>
<td>1</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
<td>122</td>
<td>20</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
<td>10</td>
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<td>10</td>
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<tr>
<td>4</td>
<td>4&lt;sup&gt;th&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
<td></td>
<td></td>
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<td></td>
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</table>

Table 3: Resin/Fibre Formulations for the Casting of Thermosetting Seat

<table>
<thead>
<tr>
<th>S/N</th>
<th>Laminate</th>
<th>Mass of Resin (g)</th>
<th>Mass of Fibre (g)</th>
<th>Mass of Gelcoat (g)</th>
<th>Mass of Blue Pigment (g)</th>
<th>Mass of Catalyst (g)</th>
<th>Mass of Accelerator (g)</th>
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<td>1&lt;sup&gt;st&lt;/sup&gt; Laminate</td>
<td>503.30</td>
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<tr>
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<td>2&lt;sup&gt;nd&lt;/sup&gt; Laminate</td>
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<td>250.40</td>
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<td>10</td>
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<tr>
<td>3</td>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
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<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>4&lt;sup&gt;th&lt;/sup&gt; Laminate</td>
<td>503.30</td>
<td>250.40</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Determination of the Tensile Strength of the Dumbbell Shapes of the Laminates

The tensile test of the laminates was determined using a Monsanto tensometer (type ‘w’) S/no 9875. The test was done using the ASTM D5083 standard for reinforced and unreinforced plastics. The unreinforced plastics (100% matrix) was used as the control sample while the various laminate were also tested.

Test procedures: The various dumbbell shapes of the laminates were cut and fixed on the Monsanto device. The various indentations on the Monsanto graph sheets were noted at the point of rupture. The breaking force and elongation/ultimate tensile strength/modulus of the various laminates were calculated.

Determination of the Flexural Strength of the Laminates

The flexural strength of a composite is the maximum tensile stress it can withstand during bending. This was done in accordance to the ASTM D790 using the Monsanto device. The Monsanto tensometer (type ‘w’) S/No 9875 was adjusted and a “flexural fixture “attachment” was fixed and the specimen attached to it. As the Monsanto spindle was rotated, the mercury on the beam glass moves as the indentations were made on the Monsanto graph sheet. The specimen stopped bending immediately the mercury on the side glass stopped moving. Then the spindle rotation was stopped also.

The force/stress required to bend the specimen and the deflection were calculated from the dots in the graph using the appropriate scales.

Hardness Test

The hardness of the laminates was performed to determine or ascertain the degree to which the materials will withstand indentation or scratch. This was done according to ASTM D2240. The test was done with the aid of a Durometer considering the ASTM D2240. This test measures the penetration of a specified indenter into the laminate.

The various laminates were placed on the surface below the indenter of the Durometer. Starting with the control sample, the indenter was then pressed against the test piece (that is after the indenter was set to the zero mark) using the handle of the machine the reading was taken. The procedure was repeated three times for other laminates and the average of the various readings were taken in shore.

Scanning electron microscopy (SEM)

This is the most widely used type of electron microscope. It examines microscopic structure by scanning the surface of the laminates An SEM image is formed by a focused electron beam that scans
over the surface area of the specimen. The sample was cut 2/2 centimeter square and was placed on a double adhesive and placed in a sputter cater model qR50-ES made by Quoran where 5nm of gold was deposited on the sample (This is to make it electrically conductive) There after the sample was introduced into the same machine which was viewed via a navigation camera (NAV CAM) which focusing and brightness were adjusted. There after it was moved to SEM mode in which different magnifications were taken which was stored in a USB stick.

**The water absorption test**

The water absorption was used to determine the amount of water absorbed under specified conditions. The factors affecting water absorption include the type of Polymer, the additives used as a processing aid, the temperature and the period of exposure to water or moisture. The various laminates with the control sample were immersed in a normal water laboratory beaker for 72 hours under a room temperature in accordance to ASTM Test standard (ASTM D750 Standard) for water absorption.
RESULTS

Figure 5: Bending stress Vs deflection

Figure 6: Stress Vs Strain
Figure 7: Tensile modulus vs Laminate Compositions

Figure 8: Hardness Vs compositions
Figure 9: Flexural modulus Vs compositions

Figure 10: Water Absorption/Laminates
Plate I: 1000x magnification Control Sample

- Complete Cross-linking of the matrix
- Matrix Pull out (No cross-linking)
- Area of delamination

Plate I: 1000x magnification Resin with glass Fibre

- Good adhesion /crosslinking region, (no stress concentration)
- Partial pull out of the matrix/debonding
Figure 11: The Casted Thermoset Mould

Figure 12: Thermoset Plastic Seat Casted from the Mould
DISCUSSION

Figure 13: The inside View of the Thermoset Mould

Figure 14: Dumb Bell Shape of the Laminate
Strength and stiffness are probably the most important of all properties when considering whether a material is suitable for use as a composite. The strength of a material obviously dominates the determination of the collapse load of a composite. Stiffness is vital to ensure that composite structures do not deflect too much under load.

The test specimen is a dumbbell coupon as shown above. It is shaped on this way so that it will fail in the centre portion—well away from the end which are gripped in the test machine. The specimen was then placed in a tensile testing machine which pulled it until it snaps.

**Ultimate Tensile Stress of the Laminates and Modulus of Elasticity**

For some applications, the ultimate tensile strength is the useful parameter, but most polymer products are loaded well below their breaking points. Indeed, some polymers deform excessively before rupture and this makes them unsuitable for use. Therefore, for most polymer applications, stiffness (resistance to deformation under applied load) is a parameter of prime importance. Modulus is a measure of stiffness (Ebewele, 2000). In fig 5 the bending stress/deflection graph, A small stress of about 37Mpa caused an elongation of 7.37mm. the stress is higher at 100 Mpa with a deflection of 7.4mm and as the deflection is reduced the bending stress goes up. As the fibre loading increases there is a reduction in the deflection. At 300 Mpa bending stress the deflection reduces to 5.8mm.

**Stress-Strain Curve**

In fig 6 the strain increases with the control sample, but with the addition of glass fibre, there is an increase in the stress. The stress-strain curve reaches a stress value of about 138.88Mpa called the yield stress. At this point, the laminate ruptures or experience strain hardening before final failure at a stress value of about 200Mpa which is the tensile strength/elongation at break.

**Hardness Measurement**

In fig 8 The control sample has an average hardness value 86.66 shores, but with the introduction of glass fibre into the laminates, the hardness of the laminates increases even to the sixth laminates. Therefore, the rate of penetration/scratch reduces with increase in the laminates.

**Tensile Modulus**

In fig 7 The tensile modulus increases also with the control sample and as more fibre glass are impregnated on the laminates, there was an increase in the tensile modulus and with this increase, the laminates exhibits better mechanical behavior.

**Flexural modulus**

In fig 9, the flexural modulus increases with the control sample and as fibreglass were impregnated in the laminates, there was a gradual increase of the flexural modulus with the 1st, 2nd and 3rd laminates. A rapid increase was noticed in the 4th-6th compositions of the laminates.

**Scanning Electron Microscopy (SEM)**

The SEM micrographs were done for both the control sample and the laminate at 1000x magnifications respectively. At 1000x magnification, there is a better bonding of the polymer matrix. This means complete crosslinking of the matrix. The round balls on the structure for the SEM with fibre, shows fibre pull out from the laminate. At 1000x magnification, there is a far better bonding of the matrix with the glass fibre. Small holes on the region show that there was no complete crosslinking at those regions. And this could be as result of poor interfacial adhesion between the glass fibre and matrix.

**Water absorption**

From the experimental results, It was observed that the control sample and the 1st-4th laminate. but the 5th and 6th laminate absorbed 3% and 1% of water.

**CONCLUSION**

From the various results obtained from the mechanical tests the tensile, flexural hardness test, it was observed that the tensile stress/modulus of elasticity of the laminate were higher than that of control sample. The same thing was applicable to that of bending force and the flexural modulus and hardness test.
The SEM analysis was for the morphology of the control sample and the laminate. Better micrographs structure were obtained when the SEM were done at higher magnification of 1000x magnification. The water absorption on the samples showed that the 5th and 6th laminate had the least water absorption after 72hrs and the rate of absorption can equally reduce drastically if more fibre glass are impregnated into the matrix. Therefore, these laminates would be used as roofing sheets for building construction and engineering design.

REFERENCES
Sharma, B.K (2002). Industrial Chemistry. Goels Publishing house Kirshe House, Shovag Road, Meerut 25000(up) India