Effect of fillers on tensile strength of pultruded glass fiber reinforced polymer composite

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Received 13 June 2013; accepted 24 July 2014

Glass fiber reinforced polymer composite have several advantages over steel and conventional concrete structures such as high strength-to-weight ratio, good stiffness, good corrosion resistance etc. Fillers and fibers are used as reinforcing element to enhance the mechanical properties of polymer composite. In this paper effect of fillers (carbon black, bagasse fiber and calcium carbonate (CaCO$_3$) on tensile strength of pultruded glass fiber reinforced polymer (GFRP) composite has been investigated. All three fillers are mixed with each other according to design of experiment scheme and after proper mixing of these powder form fillers, from this filler mixture 15% of the resin weight is mixed in the unsaturated polyester resin matrix. Taguchi $L_9$ orthogonal array (OA) has been used for experimentation and ANOVA is used for analyse. Experiments are performed on an indigenously designed and developed pultrusion process setup. It has been observed that as the bagasse fiber content increases the tensile strength of pultruded GFRP composite increases and tensile strength reduces with the increasing content of CaCO$_3$ and carbon black. The optimum level of all three fillers are investigated and a confirmation experiment are performed which gives 291.5 MPa tensile strength of pultruded GFRP composite

Keywords: Unsaturated polyester resin, Pultrusion process, Bagasse fiber, Carbon black, Calcium carbonate, Taguchi methods

Nowadays research is aiming to develop new composites having improved strength to weight ratio and improved mechanical properties by using varied combinations of fibers and fillers with unsaturated polyester resin (UPR) which is a widely used thermo set resins for manufacturing of fiber reinforced polymer composites due to its ease of handling, molding characteristics and cured properties. Usually fillers are added to the matrix in order to improve surface finish of the composite material as surfaces without fillers could become coarse and causes decrease in mechanical properties. Particulate fillers are of considerable interest, not only from an economic viewpoint, but as modifiers especially the physical properties of the polymer. Many researchers have found that particulate fillers such as CaCO$_3$, glass fiber and carbon black are added into the polymers to improve their stiffness, elastic modulus and to reduce costs. Borkar et al. have shown in their study that addition of silica and the calcium carbonate as filler in the polyester resin matrix reduces the tensile strength in the range of 3-15% for 25-50% fillers in hand layup process. The tensile properties are affected according to fillers packing characteristics, size and interfacial bonding. The maximum volumetric packing fraction of filler reflects the size distribution and shapes of the particles. Yilmaz et al. have shown in their study that as the particle size and the %wt. of CaCO$_3$ increases the tensile strength of the glass fiber composite decreases while as particle size decreases and %wt of CaCO$_3$ in the composite increases the tensile strength of composite increases.

Tensile strength and modulus of the composites filled with carbon black and carbon fiber increase with increasing of filler contents but impact strength and elongation at break are found to be reduced.

GFRP with carbon black possesses better tensile properties than the GFRP with fly ash. On the other hand, it is also observed that the tensile properties of GFRP with filler material (fly ash & carbon black) up to 10% are not satisfactory as compared to the GFRP without filler material. According to Farag and Drai glass fiber reinforced composite made by hand layup process shows improved mechanical properties as the graphite filler content increases up to 7.5%. At this graphite filler content the ultimate tensile strength increases by 24% as compared with the unfilled composite.
The composites have many advantages over traditional glass fiber or inorganic mineral filled composites, including lower cost, lighter weight, environmental friendliness, and recyclability. Tewari et al.\textsuperscript{12} have developed bagasse-glass fiber reinforced composite material by hand lay up method with 15 wt%, 20 wt%, 25 wt% and 30 wt% of bagasse fiber with 5 wt% glass fiber mixed in resin and found that addition of bagasse fiber decreases the ultimate tensile strength. But addition of glass fiber further increases the ultimate tensile strength in comparison to commercially available bagasse based composite\textsuperscript{12}. Yong and Isao\textsuperscript{13} have used bagasse fiber as filler and reinforcing element along with glass fiber in bulk moulding compound in injection moulding improves mechanical properties of composites. This phenomenon could bring on the same effect as the glass fibers length was prolonged, so that the adhesion interface between fiber and matrix resin became larger, which leads to the increase in the mechanical properties\textsuperscript{13}. Many researcher have used fillers in hand lay, bulk moulding compound and injection moulding but there is no significant work have been seen for pultrusion process for manufacturing GFRP composites with bagasse fiber, carbon black as filler. It is a most popular method for producing continuous long profile of FRP composites. The advantages of pultrusion over other forms of composite molding are low capital and operating cost, few finishing and deflashing operations, and the better physical properties of product\textsuperscript{13,14}. This process creates continuous composite profile by pulling raw composites through a heated die. Pultrusion combines words “pull” and “extrusion” where extrusion is pulling of material such as fiber glass and resin, through a shaping die. Many resin types can be used in pultrusion including polyester, polyurethane and vinyl ester epoxy resins etc. Fiber is wetted or impregnated with resin bath and is organized and then removed of excess resin. After that the composite is passed through a heated steel die. Precisely machined and often chromed, the die is heated to a constant temperature, and may have several zones of temperature throughout its length, which will cure the thermosetting resin. The profile that exits the die is now a cured pultruded fiber reinforced plastic (FRP) composite. This FRP profile is pulled by pulling mechanism.

In this paper pultrusion process is used for manufacturing of fiber glass reinforced polymer composite along with varying composition of three fillers, namely, Bagasse fiber, carbon black and calcium carbonate (CaCO$_3$). The design of experiment using Taguchi $L_9$ orthogonal array is applied for finding the best combination of three fillers for having maximum tensile strength.

**Experimental Procedure**

An indigenously designed and developed pultrusion setup for pultrusion of FRP composite is used for experimental work. The complete pultrusion set-up for the pultrusion of test specimen is shown in Fig. 1. The whole set-up is assembled on an “H” Iron section as shown in Fig. 1 and consists of the following parts:

(i) Pre former: This is basically a cold die which gives the initial shape to fiber impregnated in the resin in resin bath it also squeeze out the extra resin from fiber.

(ii) Hot die: Multiple piece dies made of stainless steel have been used for pultrusion of strip as shown in Fig. 2. The advantage of multiple pieces die is that it can be easily opened to allow cleaning and maintenance. To avoid abrasion of die due to abrasive nature of fiber glass reinforcements, a protective surface of 25 microns thick hard chrome plating is provided. The electric heater is provided for heating the die with temperature controller. A thermocouple is set at the parting line of the die to measure and control the die temperature. Figure 2 shows the assembled pultrusion die.

(iii) Puller assembly: This assembly consists of three parts:

(a) 3 $\Phi$ AC motor – 1 HP
(b) AC drive for controlling the speed of pultrusion for 1 HP motor
(c) Gear box- speed ratio 1:60
(d) Pulling rollers: 3 sets

**Material**

(i) Unsaturated isophthalic polyester resin is used as a matrix
(ii) E glass fiber roving as reinforcement is used in this experiment
(iii) Fillers: (a) Sugar cane bagasse fiber (13.0 m in diameter and 60~30 m in length), (b) carbon black of 50 $\mu$m particle size and (c) CaCO$_3$ of 100 $\mu$m particle size
(iv) Cobalt octate of 6% concentration as accelerator
(v) Methyl ethyl keton per oxide as Catalyst
Fig. 1—Complete indigenuous pultrusion set-up (a) pultrusion process, (b) enlarged view of pulling mechanism and (c) pultruded composite coming out from hot die
Forming of compound

First of all the mixing of all three fillers namely bagasse, carbon black, and CaCO$_3$ were mixed according to the each experiment run shown in Table 2. After proper mixing of these powder form fillers, from this filler mixture 15% of the resin weight is mixed in the resin with help of blender.

The glass fiber were wetted in this resin compound bath for pultrusion E glass fiber roving bundles of 1500 mm length and 180 to 185 g in weight are formed manually to achieve the thickness of composite. After the preparation of these bundles the pulling speed of the pultrusion set-up was adjusted to 100 mm/min and the hot die temperature was kept 150°C. This setting of the set-up is kept constant during experiment. The roving bundles are wetted with resin filler compound by dipping into the resin bath and then pulled through a steel strip against the hot die; thus FRP strip of size 25×10×1500 mm is formed.

To achieve the desired thickness of composite it is required to used numbers of creels of fiber glass roving not only this a certain length of roving’s goes waste at every new start of the process. To reduce the numbers of creel, bundles of fiber roving is formed of required weight and length as shown in Fig. 3. And to avoid the wastage of fiber at each start the pulling is done in this set-up through steel strip as shown in Fig. 1c. After manufacturing the composite strip of 1500 mm length, three specimens for testing the tensile strength were prepared according to the ASTM D638 as shown in Fig. 4.

In the present study, L$_9$ Taguchi orthogonal array was used. The tensile strength data were analysed to determine the effect of the various design parameters. The experimental results were then transformed into signal-to-noise (S/N) ratio. Taguchi recommends the use of S/N ratio to measure the quality characteristics deviating from the desired values. Usually, there are three categories of quality characteristics in the analysis of the S/N ratio, viz., the lower-the-better, the higher-the-better and the nominal-the-best. Regardless of the category of the quality characteristic, a greater S/N ratio corresponds to better-quality characteristic. Therefore, the optimal levels of the process parameters have the greatest S/N ratio. The tensile strength as response falls under the category of higher-the-better type and the S/N ratio for the same can be computed as:

$$
(S/N)_{HB} = -10 \log \left[ \frac{1}{R} \sum_{j=1}^{R} \left(\frac{1}{Y_j^2}\right) \right] \quad \text{(1)}
$$

where $Y_j (j = 1, 2, ..., n)$ are the response values under the trial conditions repeated $R$ times.

Analysis of variance (ANOVA) was performed to identify the process parameters that were statistically significant. With the S/N and ANOVA analyses, the optimal combination of the process parameters was predicted. The following parameters were selected for investigating their effect on improvement in tensile strength in FRP pultrusion process:

- Fraction of (i) bagasse, (ii) carbon black and (iii) CaCO$_3$.
- Die temperature: 150°C
- Glass fiber to resin ratio is 0.80 : 1.

The design parameters as well as their chosen levels were decided as per the pilot tests and the
levels are kept within the limit so that the viscosity of resin should not reach the level where impregnation of fiber glass is difficult. Level chosen for Taguchi experiment are listed in Table 1.

Tensile tests were conducted according to ASTM D 638 on computerized universal testing machine manufactured by Fine Manufacturing Industry Miraj (Maharashtra), India. The specimens after tensile fracture are shown in Fig. 5 and the results are reported in Table 2.

To understand the experimentation the wt% of each filler in different experiments is given in Table 3.

After performing the tensile test on the specimens, a burnout test for confirmation of fiber to resin ratio is carried out. The purpose of this test is to ensure the actual percentage of the fiber content in the composite laminate. Hence, it can be used to justify whether the fiber content has compliance with the preset fiber content or not. First, a small piece of 50 g of composite is cut out from the pultruded composite for each sample. The furnace is switched on and set to 600°C. The furnace is then let to reach the desired temperature until the temperature inside the furnace is stable. After that, the small piece of composite was put in the furnace and burned at 600°C for one hour. The small piece is then moved out from the furnace after burning. The weights of pultruded specimens after burning at 600°C for 1 h are recorded and fiber content is calculated as in Table 4.

To find out the loss of mass due to burning at 600°C the calcium carbonate, bagasse fiber and carbon black were heated at 600°C for 1 h separately.

Results and Discussion

The average values of tensile strength and the S/N ratio for each parameter at level L1, L2 and L3 were calculated and are given in Table 5. These values have been plotted in Fig. 6.

From the trend of response curves for tensile strength at different levels of the process parameters,
it can be observed that when content of bagasse increases, tensile strength improves. The possible reason for this is that the short bagasse fiber provides interlocking with glass fiber and thus the later is firmly fixed in the former. This could increase the effective stress transfer at the interface. Figure 6a shows that the tensile strength of pultruded GFRP composite increases with the increasing content of the bagasse fiber.

The interlocking of glass fiber with bagasse fiber can be understand with scan electron microscope (SEM) images of specimen 3, 5 and 7 shown in Figs 7a, 7b and 7c. Due to the honeycomb structure of bagasse fiber the matrix and glass fiber embedded in bagasse fiber and produce the better reinforcement.

The tensile strength of composite decreases with increase in carbon black content. This is due to the reason that the hardness of matrix increases as the carbon black % increases and during curing process some of glass fiber filament get broken-down due to erosion this phenomena can be seen in SEM image of specimen no.7 in Fig. 7c.

The tensile strength variation of composite with CaCO$_3$ content is shown in Fig. 6c. The tensile strength of the composite increases with decrease in content of CaCO$_3$. The tensile strength of the fiber glass reinforced pultruded composite increases with the decreasing content of CaCO$_3$. The possible reason of this phenomenon is due to void formation owing to clustering of CaCO$_3$ particles. As discussed in the introduction, with the increase in % of CaCO$_3$ the tensile strength of woven FRP composite reduces, while as the size of CaCO$_3$ particles is reduced the tensile strength improves. Void are shown in Fig. 7d at place where the clustering of CaCO$_3$.

### Table 3—weight % of each filler in experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>%bagasse (N1)</th>
<th>%carbon (N2)</th>
<th>%CaCO$_3$ (N3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>4.20</td>
<td>1.80</td>
<td>9.00</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>5.52</td>
<td>1.58</td>
<td>7.89</td>
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<tr>
<td>Experiment 3</td>
<td>8.07</td>
<td>1.15</td>
<td>5.77</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>5.76</td>
<td>3.46</td>
<td>5.77</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>3.46</td>
<td>1.36</td>
<td>10.23</td>
</tr>
<tr>
<td>Experiment 6</td>
<td>4.68</td>
<td>0.94</td>
<td>9.37</td>
</tr>
<tr>
<td>Experiment 7</td>
<td>2.81</td>
<td>2.81</td>
<td>9.37</td>
</tr>
<tr>
<td>Experiment 8</td>
<td>4.50</td>
<td>3.00</td>
<td>7.50</td>
</tr>
<tr>
<td>Experiment 9</td>
<td>2.37</td>
<td>0.79</td>
<td>11.84</td>
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### Table 4—Percent of glass fiber in composite specimen

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Weight before burning (g) (1)</th>
<th>Weight after burning (2)</th>
<th>Weight of resin (3) = [(1)-(2)]/[1.15-((N1)*0.2+(N2)+(N3))/100]</th>
<th>Weight of glass fiber (g) (4) = (1)-1.15*(3)</th>
<th>% Fiber content in composite</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>25.3</td>
<td>23.9</td>
<td>22.5</td>
<td>0.45</td>
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<tr>
<td>2</td>
<td>50</td>
<td>25.0</td>
<td>23.9</td>
<td>22.5</td>
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</tr>
<tr>
<td>3</td>
<td>50</td>
<td>24.6</td>
<td>23.9</td>
<td>22.5</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>25.0</td>
<td>23.9</td>
<td>22.5</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>25.7</td>
<td>23.7</td>
<td>22.8</td>
<td>0.46</td>
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<tr>
<td>6</td>
<td>50</td>
<td>25.2</td>
<td>23.9</td>
<td>22.6</td>
<td>0.45</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>25.6</td>
<td>23.9</td>
<td>22.6</td>
<td>0.45</td>
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<tr>
<td>8</td>
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<td>25.3</td>
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<tr>
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<td>50</td>
<td>25.3</td>
<td>23.9</td>
<td>22.5</td>
<td>0.45</td>
</tr>
</tbody>
</table>

### Table 5—Average values and main effects of tensile strength of composite

<table>
<thead>
<tr>
<th>Level (tensile strength Mpa)</th>
<th>Bagasse</th>
<th>Carbon black</th>
<th>CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw data S/N ratio</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Average values</td>
<td>L1</td>
<td>268.50</td>
<td>48.55</td>
</tr>
<tr>
<td>Raw data S/N ratio</td>
<td>L2</td>
<td>231.94</td>
<td>47.30</td>
</tr>
<tr>
<td>Raw data S/N ratio</td>
<td>L3</td>
<td>224.49</td>
<td>47.00</td>
</tr>
<tr>
<td>Main effects (tensile strength MPa)</td>
<td>L2-L1</td>
<td>-36.56</td>
<td>-1.25</td>
</tr>
<tr>
<td>Raw data S/N ratio</td>
<td>L3-L2</td>
<td>-7.46</td>
<td>-0.30</td>
</tr>
</tbody>
</table>

L1, L2 and L3 represent levels 1, 2 and 3 respectively of parameters. L2–L1 is the average main effect when the corresponding parameter changes from level 1 to level 2. L3–L2 is the average main effect when the corresponding parameter changes from level 2 to level 3.
Estimation of optimum performance characteristic

The optimum value of tensile strength was predicted at the selected levels of significant parameters A1, B3 and C3 (Tables 5-7). The estimated mean of the response, i.e. tensile strength was determined as

\[ \text{Tensile strength} = T_{A1} + T_{B3} + T_{C3} - 2 T_{\text{avg}} = 293.98 \text{ MPa} \]

Where \( T_{\text{avg}} \): Overall mean of tensile strength = 241.64 MPa (Table 2); \( T_{A1} \)=Average tensile strength at the first level of bagasse content (A1) = 268.5 MPa;

\( T_{B3} \)=Average tensile strength at the third level of carbon black content (B3) = 249.56 MPa;

\( T_{C3} \)=Average tensile strength at the third level of \( \text{CaCO}_3 \) (C3) = 259.20 MPa

The 95% confidence interval of confirmation experiments (CI_CE) and of population (CI_POP) was calculated by using the following equations:

![Fig. 6—Effect of process parameters on tensile strength and S/N ratio (main effects) (a) bagasse content, (b) carbon black content and (c) \( \text{CaCO}_3 \) size](image)

![Fig. 7—SEM images showing the microstructure of specimen (a) 3, (b) 5 void due to clustering of \( \text{CaCO}_3 \) and (c) 7 broken glass fiber filaments due to erosion](image)
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The optimal values of process parameters for the predicted ranges of tensile strength are as follows:
First level of bagasse content (A1) = 35 g
Third level of carbon black content (B3) = 05 g
Third level of CaCO₃ (C3) = 25 g

Confirmation experiments
Three confirmation experiments were conducted at the optimum setting of the process parameters. The bagasse content was taken at the first level (A1), carbon black content was taken at the third level (B3) and CaCO₃ was kept at the third level (C3). These all fillers are mixed properly with each other and 15% of the resin weight of this filler mixture was mixed in resin. Then the composite strip was pultruded with this resin filler compound and keeping the resin and fiber ratio and other process parameters constant. Three specimens were cut from this strip and tensile tests were performed on universal testing machine. The average tensile strength of test was found 291.5 MPa, which was within the confidence interval of the predicated optima of tensile strength.

Conclusions
The effect of three fillers bagasse fiber, carbon black and CaCO₃ on tensile strength of the fiber glass reinforced composite was investigated. The following conclusions can be drawn from the study:
(i) The tensile strength at the optimum levels of bagasse fiber, carbon black and CaCO₃ is 291.5 MPa.
(ii) It is possible to enhance the tensile strength of the composite by using smaller particle size of CaCO₃ and carbon black.
(iii) Experiments on pultrusion of fiber glass reinforced polymer composite test pieces confirm that as the bagasse fiber increases the tensile strength increases within the testing levels and tensile strength decreases with the increasing contents of carbon black and CaCO₃.
(iv) The predicted optimal range for tensile strength is CI_pop: 290.2< tensile strength<297.76
(v) The 95% confidence interval of the predicted mean for tensile strength is 288.27< tensile strength<299.71

References

<table>
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<th>Table 6—Pooled ANOVA (raw data)</th>
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<tbody>
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</tr>
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<td>Bagasse</td>
</tr>
<tr>
<td>Carbon black</td>
</tr>
<tr>
<td>CaCO₃</td>
</tr>
<tr>
<td>Error</td>
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<td>T</td>
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</tbody>
</table>

*Significant at 95% confidence level
SS: sum of squares; DOF: degrees of freedom; V: variance; P: percent contribution

<table>
<thead>
<tr>
<th>Table 7—Pooled ANOVA (S/N data)</th>
</tr>
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<tbody>
<tr>
<td>Source</td>
</tr>
<tr>
<td>Bagasse</td>
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