# Effect of fillers and low profile additives on the bending of pultruded composites

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## Abstract

This paper deals with the effect of fillers and additives on the mechanical properties of pultruded composites. Six materials with varying filler and low profile additive (LPA) content have been manufactured by pultrusion using E-glass fiber reinforcement roving in a general purpose unsaturated polyester resin. The materials were pultruded in the form of a 50x6.4 mm rectangular cross-section profile. The mechanical tests consist of three-point-bending tests according to the ASTM D2344 Standard for short beam shear tests and the ASTM D739 Standard for flexural tests. Additional tests were performed at other span-to-depth (L/h) ratios varying from 5 to 24. The test results are analysed to serve two different objectives. The first objective consists in determining the effect of fillers and LPA content on the mechanical behaviour. Within this respect, it was found that an increase in the filler content form 20 to 40% results in a small decrease in the shear strength while the flexural strength seems insensitive. The addition of LPA from 5 to 20% reduces the shear strength without affecting the flexural strength. The second objective consists in determining the possible misinterpretation of three-point-bending standard tests. The results of this investigation show that, for some of the materials investigated, a clear shear fracture was obtained with an L/h ratio of 11 instead of L/h=5 as recommended by the ASTMD 2344 standard. Actually, for small L/h ratios, the fracture is preceded by a plastic flow of the specimen side under compression. This behaviour is more pronounced for the materials containing LPA.

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# 1 Introduction

High volume production of low cost Fiber-Reinforced Plastics (FRP) unavoidably requires the use of additives and fillers. Generally, additives and fillers are used to improve the surface quality of the part, alleviate some processing problems and reduce the overall cost. Since in the case of un-reinforced plastics additives and fillers are known to knock down the mechanical performance, by extension, this reality has led to believe that they have the same drawbacks on FRP's. This may be true in some circumstances; however, it is also true that if used *properly* with FRP's, the advantages of fillers and additives can considerably overcome their drawbacks. Actually, even for adhesives it was shown that an adequate choice of fillers at optimal contents could significantly improve their performance [1].

Fillers such as calcium carbonate ($CaCO_3$) and kaolin ASP400 (clay powder) are the most commonly used fillers in low cost FRP's. In the pultrusion process, as in this investigation, fillers are used to prevent the adhesion of the resin to the die, to lower the magnitude of the exothermic peak responsible for internal cracking in thick pultruded parts, and to increase the line speed and hence the productivity. Pultrusion is comparable to the extrusion of plastics and is a continuous manufacturing process intended to produce profiles with constant cross-sections. Low profile additives (LPA) are thermoplastics partially compatible with unsaturated polyester resins (UPE) before the cure. LPA are added to unsaturated polyesters in order to control the shrinkage during the cure and hence, improve the surface aspect. Such characteristics are mostly required in the automotive industry where the surface aspects are of primarily importance. The most studied and industrially used LPA with UPE resins is the Poly(Vinyl Acetate) (PVAc). Huang and Chen [2], performed a long term study dealing with styrene/UPE/low profile additive ternary systems. Gordon et al [3] investigated the effect of PVAc on the cure kinetics and surface aspects of RTM moulded parts. It was observed that the heat generation as measured by differential scanning calorimetry (DSC) tests varies with varying the PVAc content and this variation displays a clear transition that has been correlated with the surface roughness and microscopic observations of the morphology. The same LPA as in [3] is used this investigation.

# 2 Experimental procedures

## 2.1 Materials

This study has been conducted on six materials with varying filler and LPA (Low Profile Additive) content. The filler used is the ASP400 (clay powder) with a mean size value of 4.8 μm. The LPA used is the LP-40A from Union Carbide which is constituted of 40% PVAc and 60% Styrene. Three filler contents (B: 20%, C: 30% and D: 40%) and four LPA content (B: 0%, TA: 10%, TB: 15%, TC: 20%) have been used. These materials were manufactured in our laboratory by pultrusion using a general purpose unsaturated polyester resin reinforced with

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unidirectional E-glass fibers. The fiber volume content FV was maintained constant at 51.6% for all the materials investigated. The pultruded profile is a rectangular cross-section of 6.4X50 $mm^2$. The investigation of the effect of fillers and LPA was limited to the mentioned contents because for FV=51.6, it was not possible to pultrude the profiles without fillers. This phenomenon is due to the fact that pultrusion is only possible above a critical amount of solid content. Actually, it is possible to pultrude profiles with higher FV, however; the higher volume fraction will not allow the use of high fillers and/or LPA content. For these reasons, the material with 20% filler content is used as the reference material for both the effect of fillers and the effect of LPA.

### 2.2 Testing

The flexural specimens for the effect of fillers were tested as moulded i.e. with a width of 50 mm and a thickness of 6.4 mm. The flexural test specimens for the LPA effect were machined from the pultruded profiles with a width of 13 mm while keeping the original thickness. The tests were performed in a three point bending fixture that allows the change of the distance between the two support points (span). The tests were performed at five span (L) to thickness (h) ratios (L/h = 5, 6, 11, 16 and 24). The three-point-bend tests at L/h = 5 and 16 are respectively in accordance with ASTM D2344 [4] and ASTM D790 [5] standards for the determination of the shear strength and flexural strength. The specimens are loaded at the mid-span of the upper surface. The maximum tensile stress prevailing in the extreme fibers of the lower surface ($\sigma_{11}$) and the maximum shear stress prevailing at the neutral plane ($\tau_{31}$) are calculated using the beam theory. All the tests are performed on a servohydraulic MTS machine model 810 equipped with a Teststar II module and software for control and data acquisition.

## 3 Results and discussion

In the bending mode both normal stresses and shear stresses are present throughout the beam span [6]. According to the beam theory, high L/h ratio favour normal stresses ($\boldsymbol{\sigma_{11}}$) and low L/h ratio favour shear stresses ($\boldsymbol{\tau_{31}}$). The ASTM D790 standard [5] assumes that an L/h $\geq$ 16 produce a failure on the tension side and the maximum fiber stress reached during the test can be considered as the flexural strength $\boldsymbol{\sigma_{11}}^*$. The ASTM D2344 [4] assumes that for glass fibers, an L/h= 5 produce a shear failure and the maximum shear stress $\boldsymbol{\tau_{31}}^*$ can be considered as the interlaminar shear strength (ILSS). Even though, the limitations of these two standards are known since three decades, these tests are the most used by the pultrusion industry. Beside the fact that these tests are cost effective and easy to perform, the other justification is that pultruded profiles are usually used in applications were bending is the predominant loading mode. To highlight the mentioned limitations of the standards in determining the effect of fillers and LPA additives, we have chosen to extend the tests on five L/h ratios (5, 6, 11, 16 and 24). Actually, such extension on many different materials gives an additional opportunity to discuss the limitations of the two standards. All the

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flexural tests results dealt with in this investigation are presented in Table 1. The results of Table 1 have to be discussed horizontally to see the effect of the filler and LPA content for each L/h ratio and vertically to see the variation of the shear and flexural strengths as function of the L/h ratio. However, we first discuss the effect of rigid fillers and then the effect of LPA additives.

Table 1: Effect of fillers and LPA on the flexural properties. $E_f$ is the flexural modulus.

| | | Filler effect<br>Width = 50mm | | | LPA effect<br>Width =13mm | | | |
|---|---|---|---|---|---|---|---|---|
| L/h | Property | ***B*** ***20%*** | C 30% | D 40% | ***B*** ***0%*** | TA 10% | TB 15% | TC 20% |
| 5 | $\tau_{31}^*$ MPa | ***52*** | 50 | 47 | ***53*** | 52 | 49 | 44 |
| | $d_u$ mm | ***0.89*** | 0.88 | 0.80 | ***0.69*** | 0.8 | 1.16 | 1.11 |
| 6 | $\tau_{31}^*$ MPa | ***47*** | 45 | 43 | ***49.9*** | 48.06 | 46.55 | 41.9 |
| | $d_u$ mm | ***1.05*** | 1.01 | 0.92 | ***0.91*** | 0.93 | 1.17 | 1.09 |
| | | | | | | | | |
| 11 | $\tau_{31}^*$ MPa | ***43*** | 40 | 39 | ***43*** | 42 | 38 | 32 |
| | $\sigma_{11}$ MPa | ***909*** | 842 | 820 | ***948*** | 888 | 804 | 701 |
| | $d_u$ mm | ***3.18*** | 3.00 | 2.92 | ***3.22*** | 3.21 | 3.15 | 2.89 |
| | | | | | | | | |
| 16 | $\sigma_{11}^*$ MPa | ***1135*** | 1100 | 1088 | ***1034*** | 1092 | 985 | 874 |
| | $E_f$ GPa | ***39.36*** | 39.60 | 40.12 | ***38.95*** | 38.84 | 37.04 | 35.55 |
| | $d_u$ mm | ***8.17*** | 7.81 | 7.74 | ***7.52*** | 7.69 | 7.19 | 6.56 |
| 24 | $\sigma_{11}^*$ MPa | ***1072*** | 1062 | 1073 | ***1096*** | 1093 | 1052 | 1090 |
| | $E_f$ GPa | ***39.91*** | 39.77 | 39.69 | ***41.39*** | 39.97 | 39.55 | 40.49 |
| | $d_u$ mm | ***17.39*** | 16.90 | 16.54 | ***17.81*** | 17.74 | 17.09 | 17.08 |

### 3.1 Effect of fillers

The effect of fillers is shown in Table 1 on the first five columns for materials B, C and D. During the tests, it has been noticed that the specimens tested at L/h=5, 6 and 11 fail in an interlaminar shear mode. Actually, for L/h=5 and 6, the interlaminar fracture is preceded by a compressive yielding under the central

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loading nose. However, the yielding disappear for L/h= 11 and in this case a clear shear fracture is observed. The same observation is made for the three filler contents investigated. Table 1 shows that for a given L/h (5, 6 or 11), the shear strength decreases slightly as the fillers content increases. In terms of L/h effect, examination of the load-displacement (P-d) curves for different L/h shows that the P-d curves seem to become more linear as L/h increases. This is illustrated by typical P-d curves in Figure 1 for L/h=6 and 11. For L/h=11, the load drop after the maximum load is characteristic for a shear fracture. The question to be asked is: which L/h really gives representative interlaminar shear strength since a shear fracture is observed for each case?

The (P-d) curves for different filler contents also show that the ultimate displacement at maximum load ($d_u$) decreases slightly as the filler content increases. It is clear and expected that the fillers have detrimental effect on the shear strength and on the ultimate displacement. However, the extent of the decrease has to be adequately quantified. Table 1 show that an adequate quantification of the effect of fillers should absolutely be made at the same L/h ratio otherwise the extent of the decrease will be overestimated. It should be noted that the version of the ASTM D2344 standard before year 2000 [7] recommends L/h=5 wile the new version of the standard [4] recommends L/h=4.

For L/h=16 and 24 the specimen failure corresponds to a tensile fracture of the fibers on the tension side. The difference in the flexural strength values for the two L/h obtained is almost within the results scatter. Consequently, the maximum stresses at both L/h=16 and 24 are representative of the flexural strength. For L/h=16, the filler effect is within the results scatter and for L/h =24, there is no any filler content effect.

### 3.2 Effect of low profile additives

The effect of LPA is shown in Table 1 on the last four columns. It should be reminded that the reference material for the effect of LPA additives is the material “B” containing 20% fillers (0% LPA). For the tests performed at L/h=5, the material TA with 10% LPA undergo compressive yielding; however the final fracture proceeds by interlaminar shear. The shear strength does not seem to be affected by this amount of LPA. For the materials TB and TC containing 15 and 20% LPA, the fracture proceeds by extensive compressive yielding under the loading nose and no clear interlaminar fracture is observed. While the load carrying capability of the material is slightly diminished; the ultimate displacement at fracture $d_u$ increases with the LPA content increase. For L/h = 6, the extent of the compressive yielding diminishes and a mixed compressive/shear fracture is observed. Again, the load carrying capabilities of the material decreases. For L/h= 11, shear failure is dominant and as it can be seen form Table 1, while the 10% LPA does not seem to affect the shear strength; the 20% LPA decreases the shear strength by about 26% and surprisingly, even the ultimate displacement at maximum load ($d_u$) is diminished. A readily apparent explanation of this behaviour is that the void content increases significantly above a critical amount of LPA. This critical LPA amount is dictated by morphological changes known as phase inversion [3].

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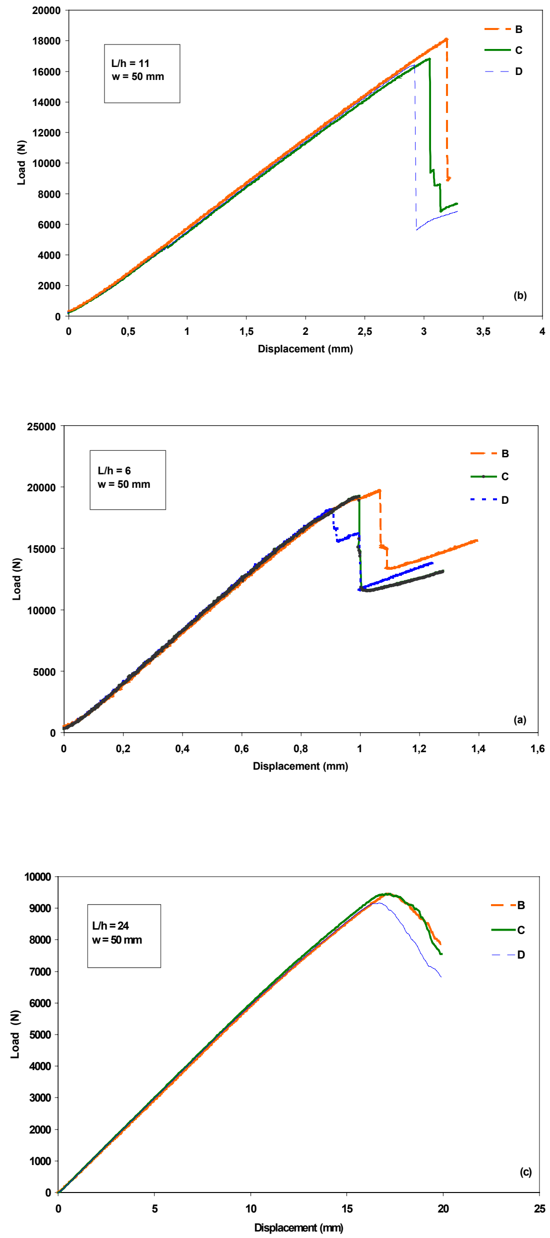


Figure 1: Effect of fillers on the three-point-bending behaviour of pultruded glass/polyester composites.

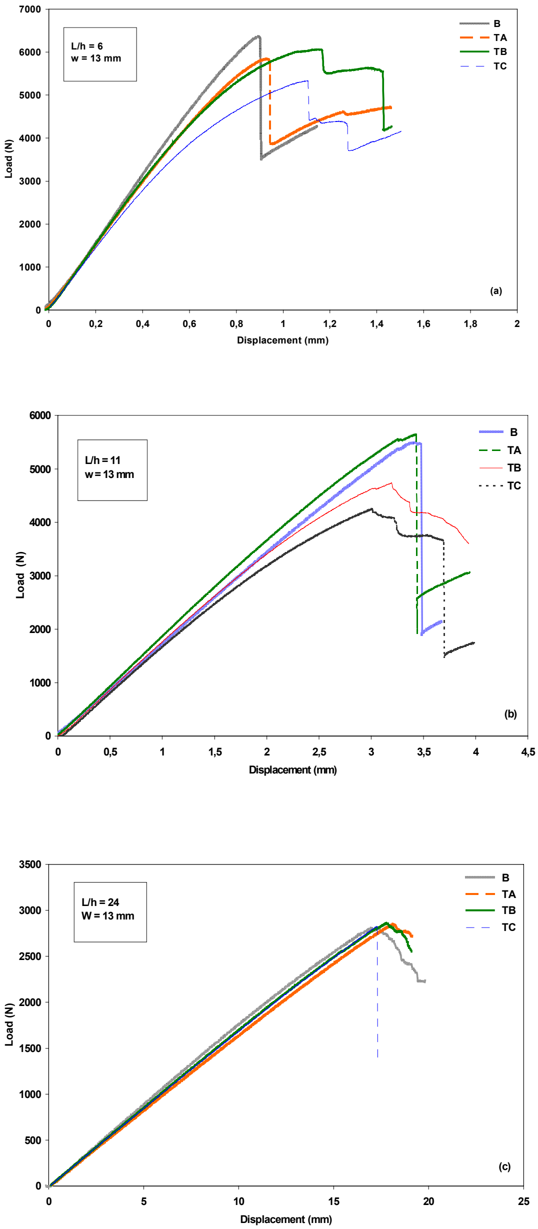


Figure 2: Effect of low profile additives on the three-point-bending behaviour of pultruded glass/polyester composites.

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At L/h=16, a mixed shear/tension failure is observed. For the material containing 10% LPA, most of the specimens fail in tension. However, when the LPA content is increased, the proportion of the specimens failing in tension decreases and mixed failure shear/tension prevail. From Table 1, it can be seen that the flexural strength calculated at L/h =16 decreases significantly with increasing the LPA content. However, since the fracture is mixed, the calculated value cannot be quoted as the flexural strength but rather as an apparent flexural strength. At L/h = 24 all the specimens fail in tension and the flexural strength is not affected by the LPA content (within the range investigated). These tests at L/h = 24 show that when the fracture proceeds by fiber tension as it should be expected from a flexure test, no LPA effect is observed. This is a good indication that the tests at L/h = 16 are not representative of the flexural strength.

Examination of the load-displacement (P-d) curves for different L/h shows that the behaviour is clearly non-linear for L/h =5 and 6. Some non-linearity is observed even at L/h=11 and the non-linearity increases as the LPA content increases as it can be seen on Figure 2. However at L/h=24, the behaviour is essentially the same as that observed for the effect of fillers.

### 3.3 Effect of span-to-depth ratio

As it can be seen from Table 1, the lowest carrying load capabilities for all the materials investigated is experienced at an L/h =11. For this case, Table 1 gives the maximum shear stress and the maximum flexural stress corresponding to the maximum failure load. In other terms, if a beam is loaded at this span-to-depth ratio, it will fail at a load lower than what can be expected from the standard shear strength or from the standard flexural strength. Boukhili et al [8] have reported similar behaviour previously for other materials including pultruded epoxy/glass composites.

Finally, it can be noted from Table 1 that the material B containing 20% fillers (reference material) has been tested at two widths (50 mm and 13 mm). As it can be seen, there is no width effect even though the 13 mm width is machined.

## 4 Concluding remarks

From the open literature, it is easy to understand the mechanisms by which fillers and additives influence the overall properties of ***un-reinforced*** resins. However, most of this literature overlooked their influence in the case of ***Fiber-Reinforced*** Plastics (FRP). This probably comes from the fact that generally, for structural applications the use of fillers is avoided if not simply banned as in the case of aeronautical applications. The numerous new applications of FRP's (transportation, electrical, civil engineering, commodities, etc.) require high volume production and low cost of fiber-reinforced composite materials. This cannot be achieved without an extensive and rational use of additives and fillers. However, the optimal use of fillers and additives require mechanical testing and the mechanical tests on which most industrial engineers rely on are flexural tests

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for obvious reasons. If not analysed with care, the results from these tests can be misleading.

The objective of this paper was twofold. (1) To show the extent by which fillers and additives affect the flexural properties in general purpose FRP's and (2) to show the limits of standard tests in providing a rigorous comparison basis.

Concerning the first objective, these results mean that even though the strength of the un-reinforced plastic can be dramatically lowered by the addition of fillers and LPA; the fiber reinforced plastic is slightly affected for short beams and almost insensitive for long beam. Actually, this means that the use of fillers and LPA additives in pultruded products provides manufacturing and cost benefits that above all exceed their drawbacks.

Concerning the second objective; clearly, the standard short beam and flexural tests are attracting, however, their interpretation need to be adjusted depending on the material under investigation. The old ASTM D2344 standard for the short beam shear test [7] advises for an L/h ratio of 5 for glass fiber reinforcement and the newest approval [3] advises for an L/h ratio of 4. This investigation and previous ones show that unidirectional pultruded composites fail by shear at lower loads than those based on the standard requirement. Actually, we recommend that the L/h ratio should be adjusted according to the compression strength of the material.

Finally, it appear from this investigation that in order to obtain a meaningful flexural strength, the flexural tests should be performed at L/h = 24. Ideally, any datasheet reporting the flexural strength and the interlaminar shear strength according to these two standards should clearly identify the L/h ratio used and the effective failure mode observed.

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