Versatility of Long Fiber AP Nylon CR-6 Organosheet to overcome intrinsic short comings of Long Fiber Thermoplastics

Navraj Heer[1], Stanislav Ivanov[1], Gleb Meirson[1], Vanja Ugresic[1], Frank Henning[1], Andrew Hrymak[1], Mingfu Zhang[2]*

[1]Fraunhofer Project Centre for Composites Research @ Western University

2520 Advanced Ave, London, ON Canada N6M 0E1

[2]Johns Manville, A Berkshire Hathaway Company

10100 West Ute Ave, Littleton, CO 80127

Corresponding author: nheer2@uwo.ca*

Abstract

Automotive industry's push to use ever more long fiber thermoplastic is driven by better mechanical properties offered by the longer fiber lengths. To materialize on this advantage the industry employed various processes such as LFT-D ECM (Long Fiber Thermoplastic – Direct Extrusion Compression Molding). LFT-D ECM process has its advantage in supporting the high-volume production, but it has limitations such as variation in fiber length in the finished parts, flow induced anisotropic properties and limited fiber loading. For end-user-based industry such as automotive, safety and reliability of components is of utmost importance. Consistency in the mechanical properties of the reinforced thermoplastic material is an important aspect governing the reliability.

Johns Manville CR-6 Organosheet, a new long fiber organosheet produced via in-situ anionic polymerization of caprolactam (AP Nylon) with randomly oriented long fibers of uniform fiber length, is demonstrated in this work to address this issue of inconsistency in fiber length and anisotropy in mechanical properties. This consistent fiber lengths reduce variation in the composite's mechanical properties; and pseudo-isotropic composite materials can be produced using specific organosheet layup in molding. The in-situ polymerization process ensures a thorough resin wet-out of long fibers. The material manufacturing process also allows for considerably higher fiber loadings (>60% by wt.), thus much improved mechanical properties. The excellent flowability of Johns Manville CR-6 Organosheet during molding and the formability of the material into complex geometries are some additional features that make the material advantageous to existing glass mat thermoplastics and organosheets.

This material also displayed greater versatility via excellent co-molding ability with the LFT-D ECM material thus expanding prospective applications.

1. Introduction

Present day manufacturing in the automotive industry focuses on light weighting both for performance and better efficiency to reduce emissions. Over the years, the increased use of fiber reinforced polymer composites has facilitated this endeavor of automotive light weighting in various forms with countless advancements. The mechanical properties of these composites were at par or in some cases superior to metals, which enabled the substitution of latter with lighter composites. Both thermosetting and thermoplastic composites have niche field of applications with some overlap. Their basic function is the same where reinforcement fibers imbedded in the matrix provide extra ordinary mechanical properties, Nevertheless the two material systems are on the complete opposite end of the spectrum when it comes to the chemistry behind the formation of these composites. This is where each of them has advantages over one another. Thermoplastic materials benefit from abbreviated cycle times due to the absence of any cross linking in the matrix which increases the part production cycle time. This knack of thermoplastics has been crucial in bringing industry wide acceptability in mass production processes. More and more components which were traditionally made out of metals have been made using thermoplastic materials over the years.

Fiber reinforced thermoplastic composites get further categorized based on the length of fiber used with the polymer. The long fiber thermoplastic (LFT) composites have the longer length of fibers and impart better strength and stiffness. These properties get further tailored based on alignment of these fibers. This directional nature of the mechanical properties may or may not be desirable and it is engineered accordingly. These properties are largely influenced by the processing technology used to make LFT composites [1] [2].

2. Classification

Figure 1 provides a synopsis of classification of different processing methods to manufacture LFT composites. Glass mat thermoplastics manufacturing uses the polymer (mostly polypropylene) and polymer films to wet-out comingled glass mats with fiber lengths ranging between half an inch to two inches, which are then pressed into sheets [3]. AP Nylon CR-6 Organosheet is the focus of this study and has been explained in the sections to follow. Indirect LFT method uses pellets infused with fiber reinforcements up to 12 mm in length which is then used in injection mold the composite parts [4]. Direct Long Fiber Thermoplastic Injection Molding (LFT-D-IMC) process involves an injection molding machine where a compound of resin coming from the extruder and chopped fiber is injected into a closed mold. Direct long fiber thermoplastic extruder compression molding (LFT-D ECM) is a very robust process where a plastificate is formed directly using set of twin-screw extruders where polymer is melted and compounded with fiber roving being chopped inside the extruder itself. This plastificate is then compression molded in a mold. It is because of its robustness, easy utilization of raw materials and ability to change the material formulation during processing, that LFT-D ECM has found a solid ground in the industry and its use is ever expanding.

Nevertheless, disadvantages of LFT-D ECM technique include:

- Non-uniform fiber length distribution:

  In this process fiber roving are directly fed into a twin-screw extruder where fibers are chopped as per the distribution of cutting elements. There is a substantial amount of fiber fluff which is formed during the direct fiber roving breaking process. The portion of undesired short fiber lengths induce aberration in the overall mechanical performance [5].

- Flow induced fiber alignment:

The plastificate for LFT-D ECM is usually a log shape with varied thickness and length which is placed in the open mold to be compression molded. During the compression molding this compound of polymer and reinforcement flows into the net shape as it cools down. The long fibers tend to align in the direction of flow where they would produce better mechanical properties in the aligned direction and significant drop of properties in the orthogonal direction. A substantial amount of anisotropy in mechanical properties is created which may be desired only in fewest of the few applications.

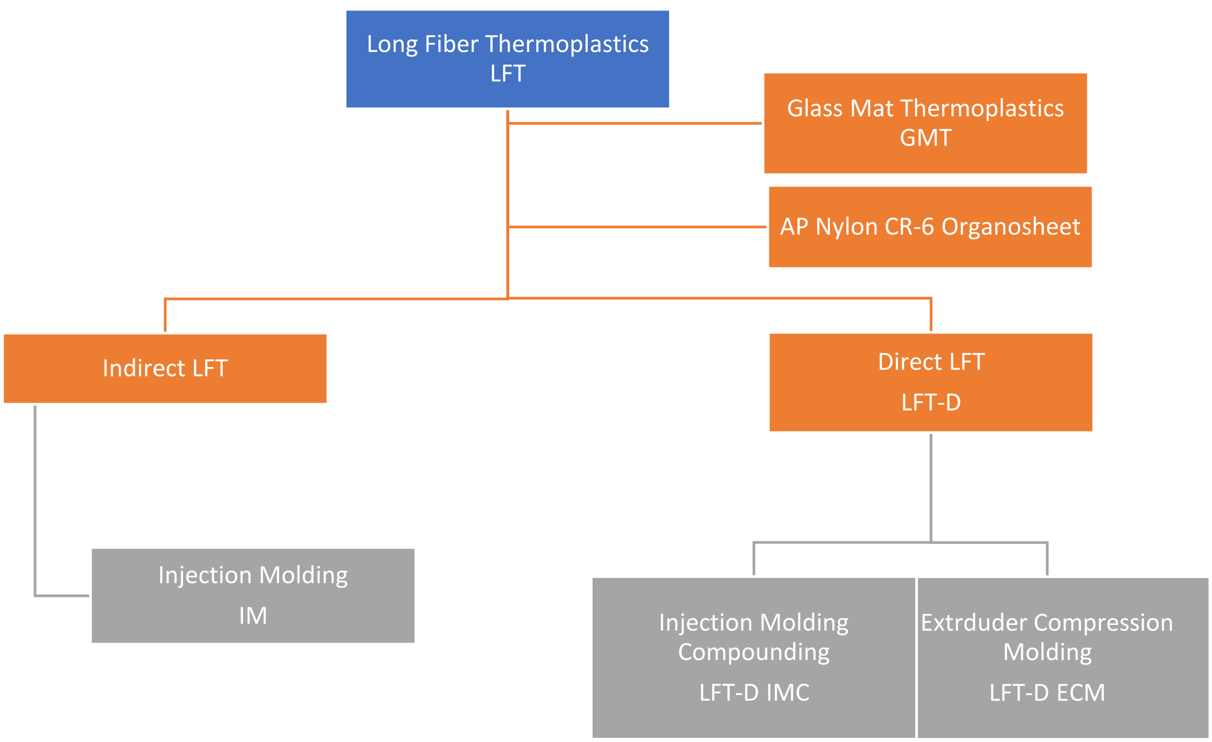


Figure 1 Classification of reinforced thermoplastic manufacturing techniques

3. Extruder Compression Molding LFT-D ECM

To corroborate on LFT-D ECM shortcomings, trials were conducted at Fraunhofer Project Centre for Composites Research at Western University London ON (FPC) to produce LFT-D material using the LFT-D ECM technique and a process to combine it with Johns Manville AP Nylon CR-6 organosheet was investigated.

3.1 Experimental trial

3.1.1 Materials:

This engineered polymer used in this study for the LFT-D ECM process was BASF's polyamide-6 (PA6) Ultramid® 8202 HS. It is an injection molding grade polymer which is compounded with heat stabilizers and has a density of 1.13 g/cc^3 and melting point of 220 °C. Fiber reinforcement used in the LFT-D ECM process was Johns Manville StarRov® 886 glass. It is a 2400 Tex roving with PA6 compatible sizing and density of 2.62 g/ cc^3.

3.1.2 Equipment:

The equipment used at FPC to produce the reinforced LFT-D ECM plaques is from Dieffenbacher which included the LFT-D ECM line supported by two twin-screw extruders and a 2500 ton hydraulic compression molding press (Figure 2). An 18 × 18 inch square plaque tool with chromed surface and heating provision was used to support the compression molding process.

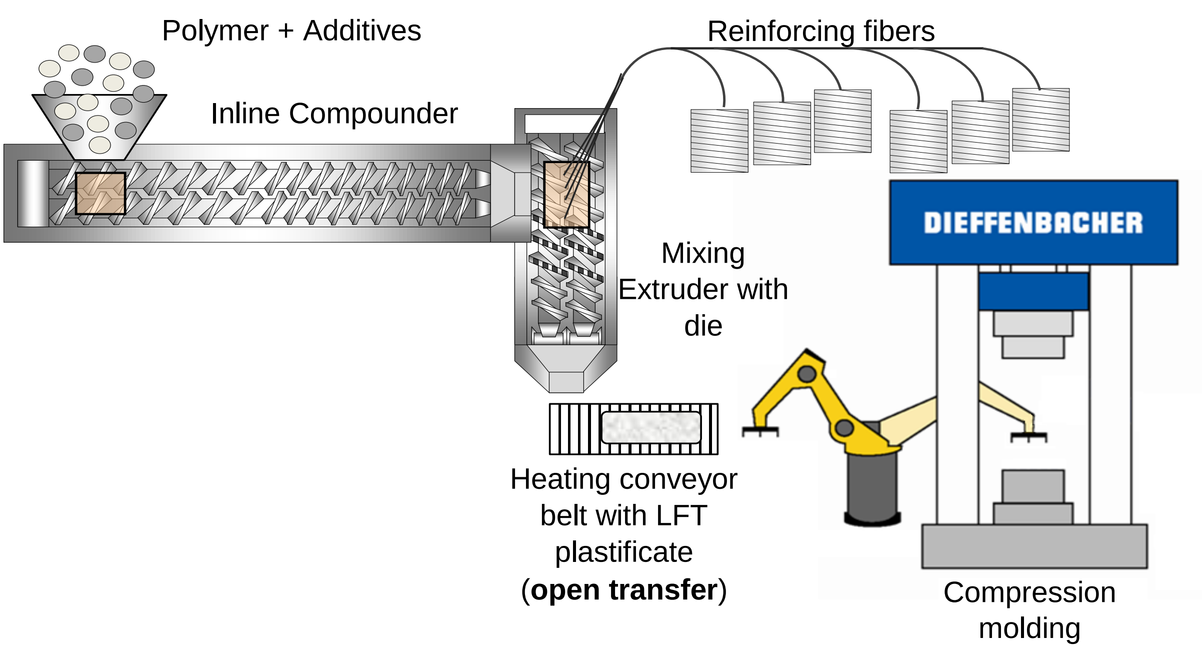


Figure 2 LFT-D ECM process schematic

3.1.3 Setup:

Equipment and materials were configured to produce 50% by weight fiber loaded plastificate at a set temperature of 270 C. 3.2 mm thick parts were made in an18”x18” square plaque to be used for mechanical testing. The mold temperature was maintained at 120 °C surface temperature. The compression cycle was 60 seconds with 150 bar set pressure.

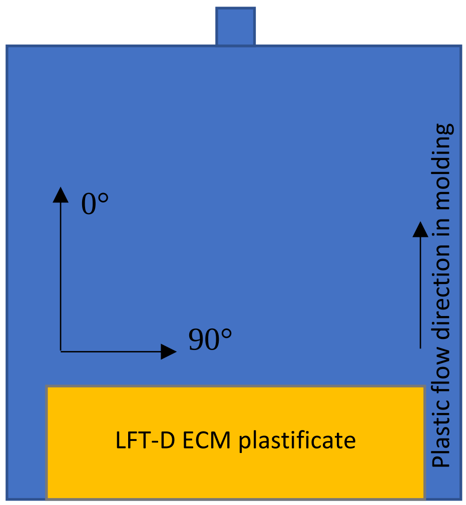


Figure 3 Plastificate placement in the mold

3.2 Mechanical testing:

3 plaques were mechanically tested with samples in in both 0° and 90° with following number of samples in each plaque:

- 10 Tensile samples each in 0° and 90° as per ASTM D 638
- 10 Flexural samples each in 0° and 90° as per ASTM D 790
- 10 Izod Impact samples each in 0° and 90° as per ASTM D 256

3.2.1 Results:

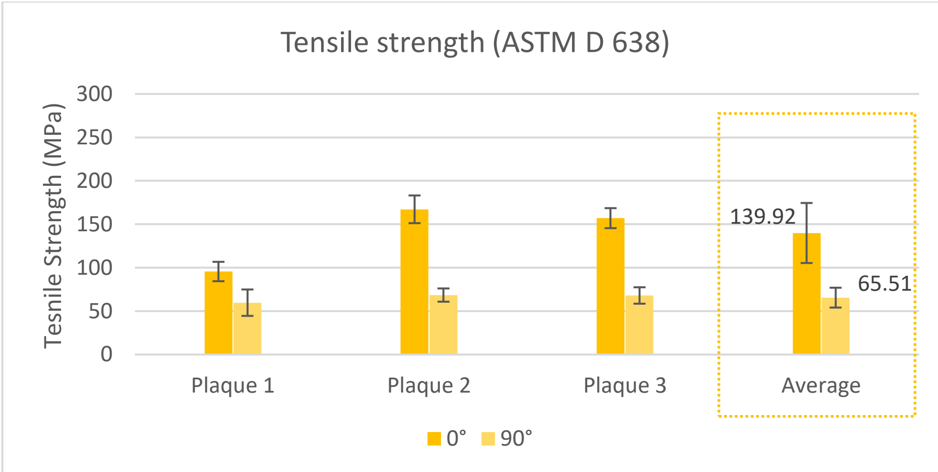


Figure 4 Shows tensile strength of the 3 plaques and their average in 0° and 90° direction

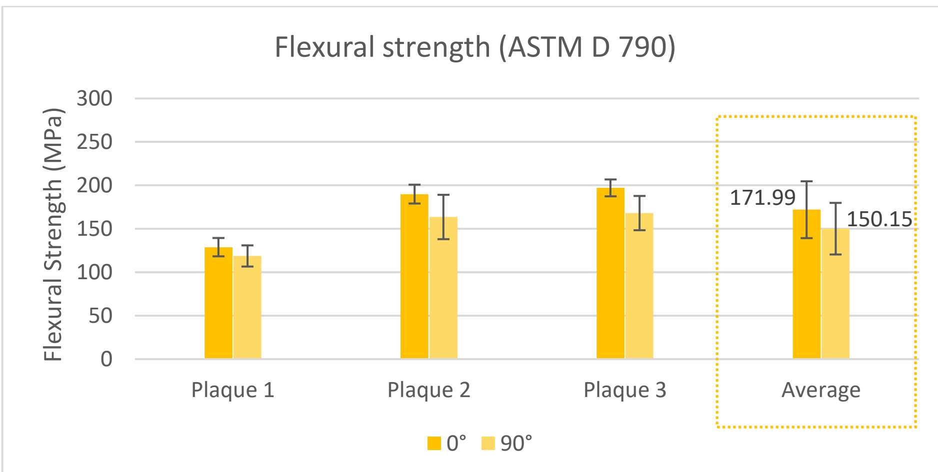


Figure 5 Shows flexural strength of the 3 plaques and their average in 0° and 90° direction

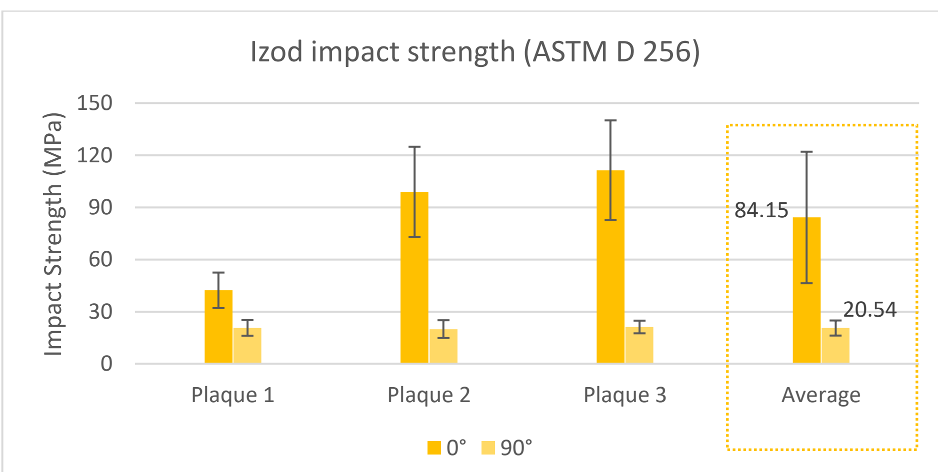


Figure 6 Shows izod impact strength of the 3 plaques and their average in 0° and 90° direction

3.2.2 Inferences from the mechanical testing results:

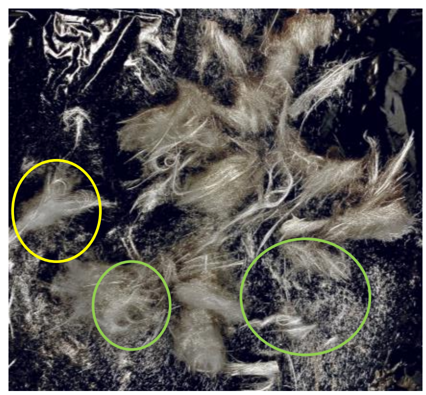
- It can be consistently noted across each of the plaque that there is noticeable amount of difference between the strength values in the 0° and 90°, where this difference is even more significant in the case of tensile (Figure 4) and impact (Figure 6) properties. This deduction confirms the severe anisotropic behavior of material in the flow region.
- Furthermore, there is significant variation in plaque to plaque values. The bigger difference being upwards of 50% between plaque 1 and plaque 3 in the case of impact strength and the least being 5%. These noticeable plaque to plaque differences in the mechanical properties and the standard deviation error bars suggest that the fiber length distribution [5] is not uniform and there are issues of fiber bundling [6].

3.3 Burn-off test:

Burn off test was conducted to see the fiber structures inside the compression molded plaque to see the glass fiber reinforcement structure inside the composite plaque (Figure 7a).

Fiber bundling (Figure 7b yellow bubble) and non-uniform fiber length distribution (Figure 7b green bubble) can be seen which have been stated in the literature before and the mechanical testing results in Figure 4, Figure 5 and Figure 6 correspond to the visuals seen from the fibers left over in the burn-off test.

a)



b)

Figure 7 a) 3.5 × 3.5 inch sample from the flow region after burn-off at 575 °C; b) enhanced picture of fibers spread out from the burn-off sample

4. Long Fiber AP Nylon Organosheet

An innovative long fiber thermoplastic composite technology, AP Nylon CR-6 Organosheet, was developed at Johns Manville to address key customer needs in automotive composite industry: strength, stiffness, consistency, and formability. CR-6 Organosheet is nonwoven thermoplastic composite sheet produced via impregnation of a randomly distributed long fiber web with caprolactam. The subsequent in situ polymerization of caprolactam forms high molecular weight polyamide-6 resin matrix and thus high-performance long fiber thermoplastic composite sheet. The uniform fiber length and random fiber distribution in CR-6 Organosheet result in more consistent mechanical properties, which increases design flexibility for automotive parts. Pseudo-isotropic composite materials can be produced using appropriate organosheet layup in molding processes. The low viscosity caprolactam resin ensures a thorough resin wet-out of long fiber reinforcement and allows higher fiber loading, resulting in better mechanical properties. Different from other thermoplastic composite sheet technologies such as glass mat thermoplastics (GMT), there is no mechanical bonding between long fibers in CR-6 Organosheet, therefore it has superior formability. CR-6 Organosheet is ideal for molding composite parts with complex shapes and deep draws.

4.1 Experimental trial

4.1.1 Materials:

The AP Nylon CR-6 Organosheet by Johns Manville with averaged 50% glass fiber loading by weight. This organosheet had consistent one inch long fibers randomly spread throughout the material with a very small amount of fiber orientation in the manufacturing machine direction (MD) which was observed in the test results to follow.

4.1.2 Equipment:

The equipment at FPC to produce the AP Nylon CR-6 Organosheet plaques were a HK Hot Air Circulation Oven and a state-of-the-art 2500-ton hydraulic compression molding press from Dieffenbacher. An 18 × 18 inch square plaque tool with chromed surface and heating provision was used to support the compression molding process.

4.1.3 Setup:

Individual AP Nylon CR-6 Organosheet have a nominal thickness of around 1.1-1.2 mm in the raw form. To make one plaque three of these sheets were stacked together and cut to squares with 17.5 inch sides. This was done to target the 3.2 mm thick 18”x18” square plaque parts to be used for mechanical testing. There is a machine direction (MD) in this organosheet, and therefore two different kind of stacks were built; 1: with MD not balanced (Figure 9 a) 2: with MD balanced(Figure 9b). The stack of Organsheets was then placed in the circulation oven set at 300°C for 10 minutes. The AP Nylon CR-6 Organosheet has been made with a heat stabilizer in the matrix resin thus producing no smoke for this prolonged heating cycle. The stack was then transferred into the square plaque mold maintained at 120 °C surface temperature. The compression cycle lasted 60 seconds with 300 bar pressure.

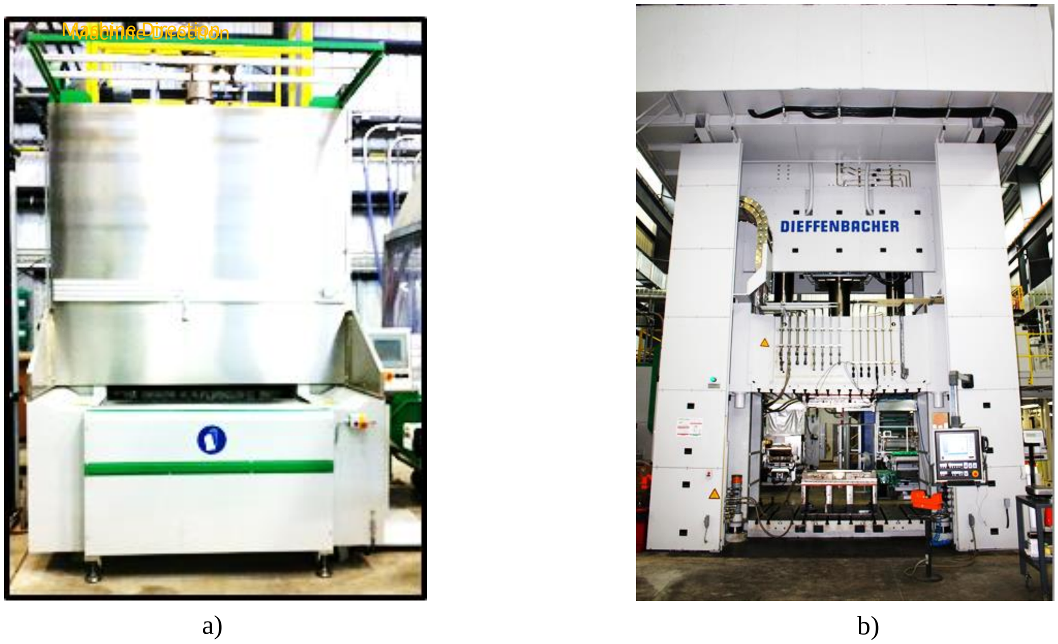


Figure 9 a) HK hot air circulation oven; b) Dieffenbacher 2500 Ton compression press

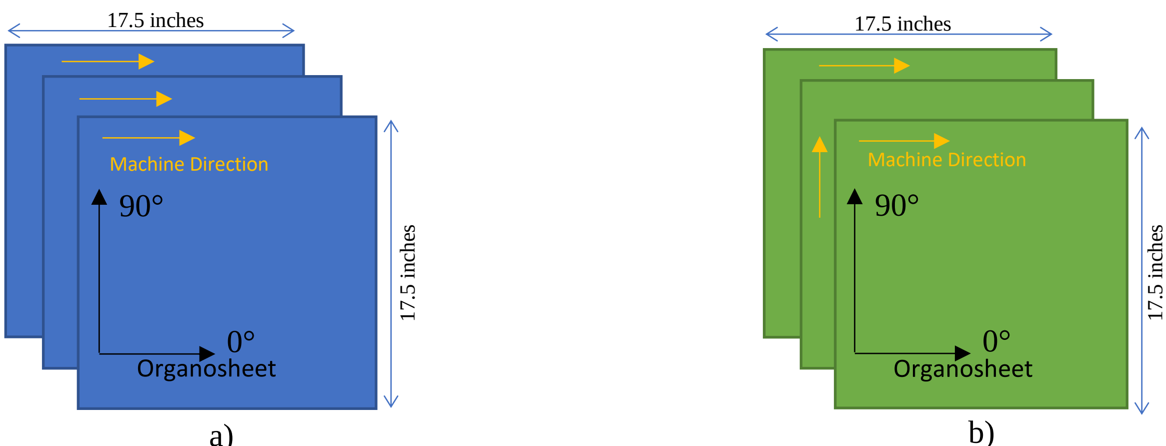


Figure 8 a) Organosheet stacking with unbalanced machine direction; b) Organosheet stacking with balanced machine direction

4.2 Mechanical Testing

3 plaques made as per the each of the stacking sequence shown in Figure 9 a and b were subjected to mechanical testing as followed:

- 10 Tensile samples each in 0° and 90° as per ASTM D 638
- 10 Flexural samples each in 0° and 90° as per ASTM D 790
- 10 Izod Impact samples each in 0° and 90° as per ASTM D 256

The 0° direction was assigned to the direction in which majority of machine direction sheets were placed in a stack as shown in Figure 9.

4.2.1 Results:

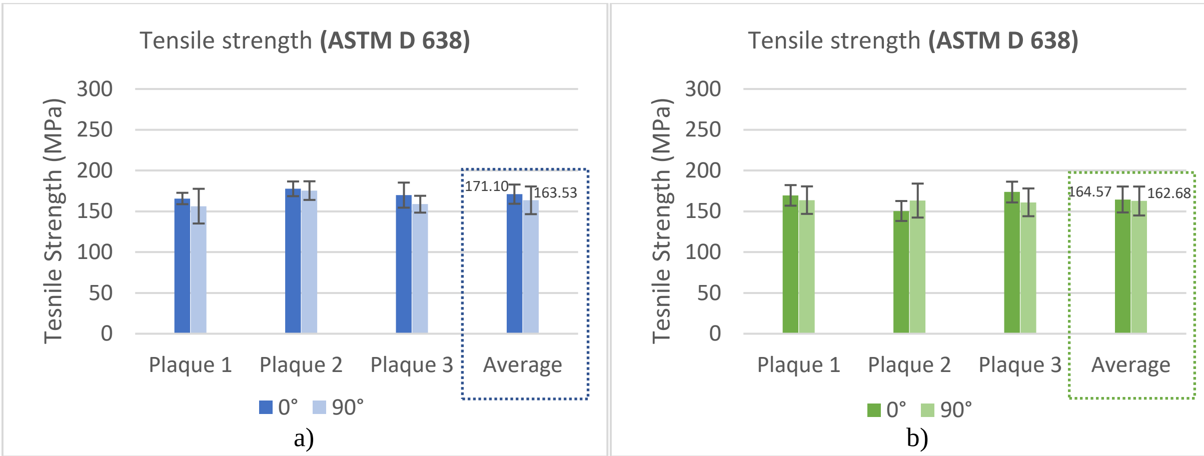


Figure 10 Comparison of tensile strength of a) 3 MD not balanced plaques and b) balanced plaques

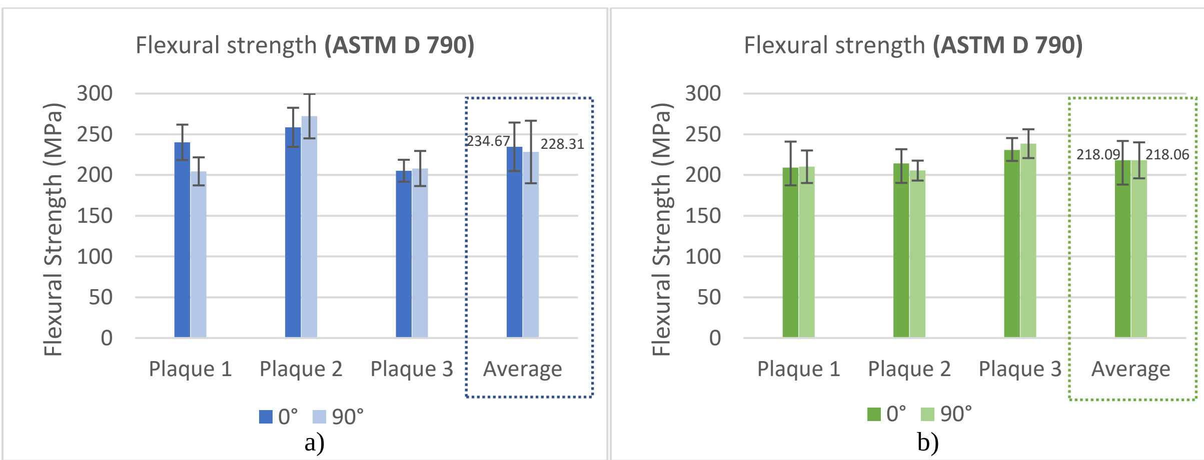


Figure 11 Comparison of flexural strength of a) 3 MD not balanced plaques and b) balanced plaques

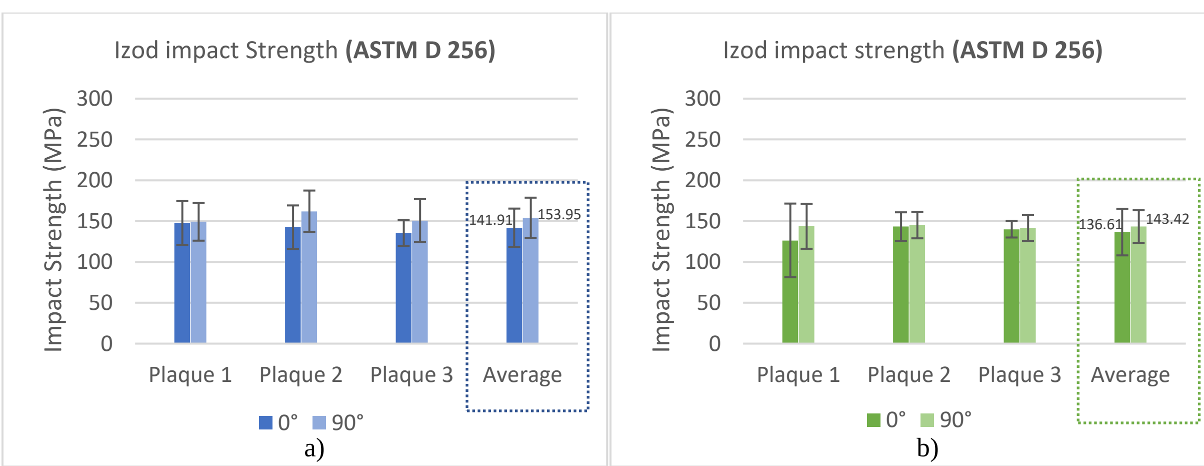


Figure 12 Comparison of izod impact strength of a) 3 MD not balanced plaques and b) balanced plaques

Contrast between averages of organosheet mechanical properties and LFT-D ECM:

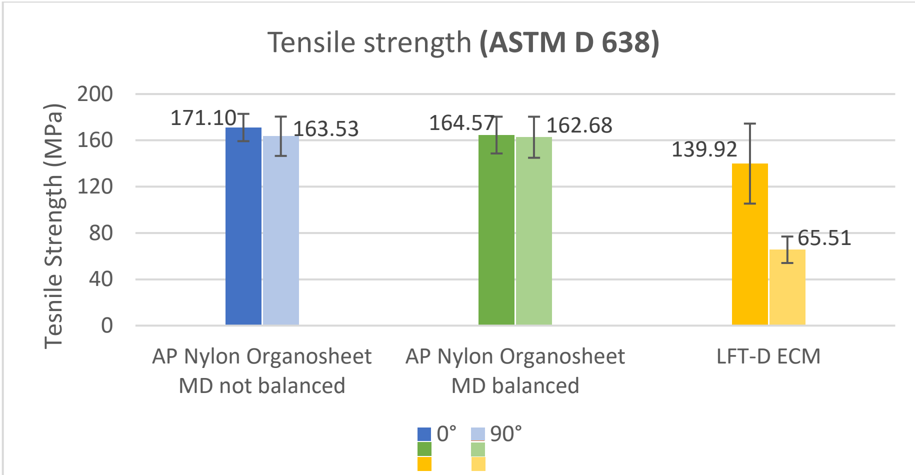


Figure 13 Comparison of average tensile strength between the two organosheet arrangements and LFT-D ECM

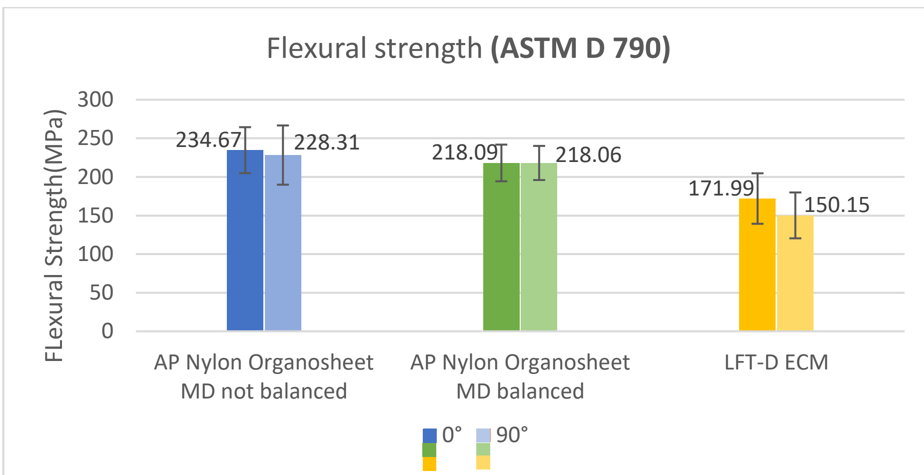


Figure 14 Comparison of average flexural strength between the two organosheet arrangements and LFT-D ECM

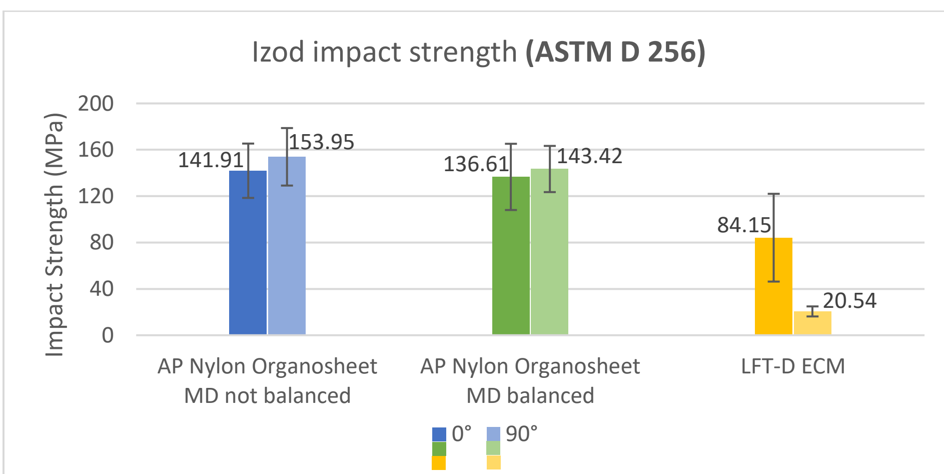


Figure 15 Comparison of average impact strength between the two organosheet arrangements and LFT-D ECM

4.2.2 Inferences from the mechanical testing results:

- Significant improvement in mechanical properties
    - It is very noticeable in the Figure 13, Figure 14 and Figure 15 that both not balanced and balance stackings of AP Nylon CR-6 organosheet plaques have a far more superior mechanical performance compared to LFT-D ECM plaques. The significance of this comparison and improved properties intensifies realizing that both composite materials systems share the same fiber loading of 50% by weight and have the same PA6 matrix material.
- Isotropy
    - The very small amount of disparity between the values of 0° and 90° all through the plots in Figure 10, Figure 11 and Figure 12 show a high level of isotropy in the material. When comparing the organosheet values and LFT-D ECM values in Figure 10, Figure 11 and Figure 12 it is even more noticeable how much isotropic behavior is demonstrated by the organosheet.
    - The MD balanced stacking of organosheet enhanced the isotropy where the difference in values of 0° and 90° was reduced. Comparing the average value averages in Figure 13, Figure 14 and Figure 15 for a quick evaluation;

      Tensile: from 4.4% difference in not balanced to 1.1% difference

      Flexural: from 2.7% to 0.01%

      Impact: from 7.8% to 4.6%.

      This removal of gap between 0° and 90° values came at a small cost of losing the peak performance which was still consistently better than LFT-D ECM performance.

- Consistency plaque to plaque
    - The plaque to plaque variation is very small throughout the plots in Figure 10, Figure 11 and Figure 12 for both MD not balanced and MD balanced cases. Thus, it can be implied that the organosheet must have a very consistent fiber length distribution throughout the material. This inference was then confirmed in the burn-off test conducted for the organosheet.
- Small standard deviation
    - Even the standard deviation bars all across the plots in Figure 10, Figure 11 and Figure 12 are much smaller when compared to Figure 4, Figure 5 and Figure 6 for LFT-D ECM which implies lesser anomalies with respect to fiber arrangement inside the plaque and also signals towards more uniform fiber length distribution

4.3 Burn-off test:

The plots in Burn off test was conducted to see the fiber structures inside the compression molded organosheet plaque (Figure 16a).

A uniform fiber length distribution (Figure 16b) and a random orientation of fibers (Figure 16a) can be seen. These visuals from the burn off confirm the trends inferred from the mechanical performance plots (Figure 10, Figure 11 and Figure 12,) for the organosheet material. From the organosheet burn-off there were absolute no fiber fluff which were seen in Figure 7b for the LFT-D ECM burn-off.

a) b)

Figure 16 a) 3.5 × 3.5 inch sample from organosheet plaque after burn-off at 575 °C; b) fibers spread out from burn-off sample

5. Co-molding LFT-D ECM and CR-6 Organosheet

AP Nylon CR-6 Organosheet demostrates superior mechanical properties due to the unique long fiber web reinforcement and the high molecular weight PA6 resin from the in-situ polymerization of caprolactam. The trade-off for this feature is the additional processing step in part manufacturing where these organosheets have to melted and formed into parts in a secondary process, thus it is not a direct process like LFT-D ECM. However, if these two materials i.e. organosheet and LFT-D ECM plastificate were carefully combined together, they can enable tailored locally enhanced mechanical properties in parts[7]. Additional experimental trials were conducted to make co-molded parts using LFT-D ECM plastificate and CR-6 organosheet. This was done to combine the benefits of two very different processing techniques and therefore to tailor locally enhanced properties.

5.1 Experimental trial

LFT-D ECM plastificate and the CR-6 organosheet were co-molded in the press together. The upstream process for both these materials were consistent with when they were processed individually. The only change was the amount of each material being put into the compression molding press. To get as close to the same part thickness of 3.2 mm for mechanical testing, a single sheet of CR-6 organosheet was used which attributed to 40 % of the weight of final plaque and rest of the 60 % of the weight was from the LFT-D ECM plastificate.

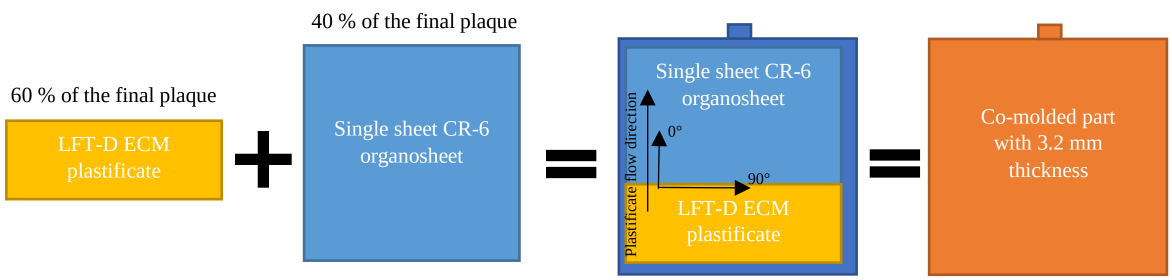


Figure 17 Co-molding of LFT-D ECM and organosheet

5.2 Mechanical testing:

3 plaques were made in a consistent way explained before and were subjected to testing with following sample arrangement:

- 5 Tensile samples each in 0° and 90° as per ASTM D 638
- 5 Flexural samples each in 0° and 90° as per ASTM D 790
- 5 Izod Impact samples each in 0° and 90° as per ASTM D 256
- 10 Short Beam Strength samples each in 0° and 90° as per ASTM D 2344

As per orientation of long fibers induced due to the flow of molten thermoplastic material (Figure 17) the 0° and 90° directions were assigned for the samples to be tested.

5.2.1 Results:

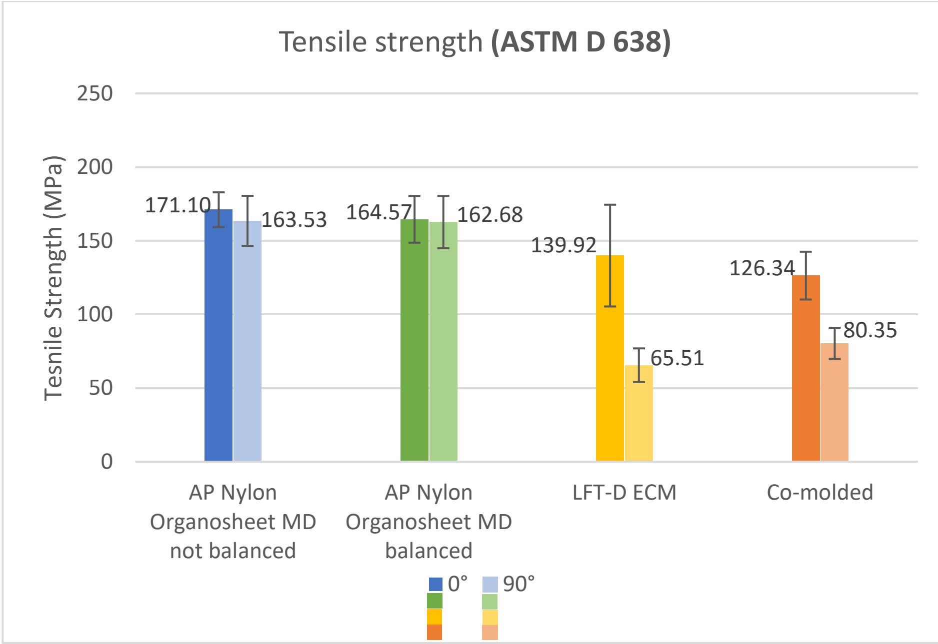


Figure 18 compares average tensile strength of the 3 co-molded plaques against organosheet plaques and LFT-D ECM plaques the 0° and 90° direction

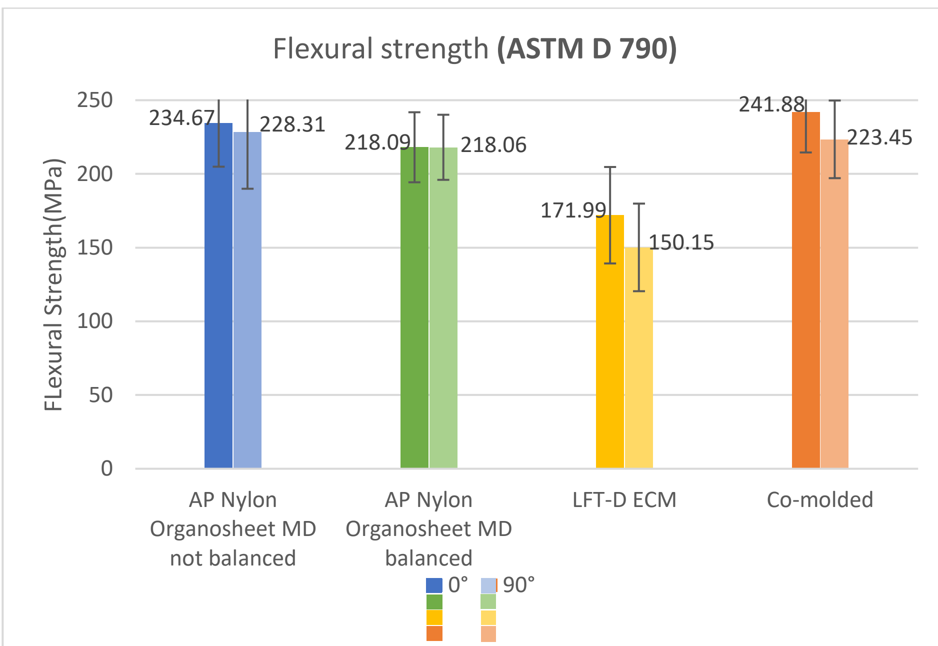


Figure 19 compares average flexural strength of the 3 co-molded plaques against organosheet plaques and LFT-D ECM plaques the 0° and 90° direction

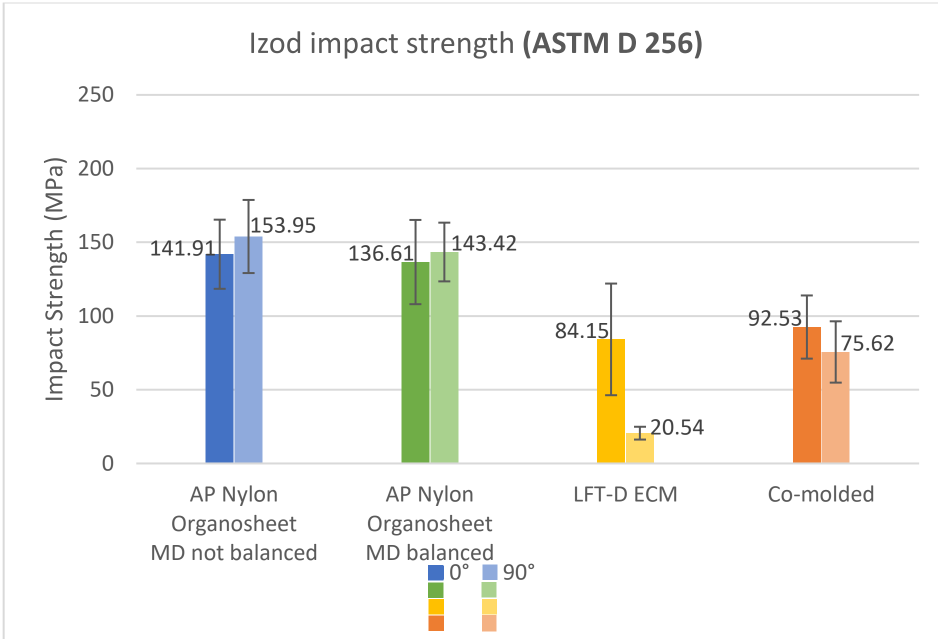


Figure 20 compares average izod impact strength of the 3 co-molded plaques against organosheet plaques and LFT-D ECM plaques the 0° and 90° direction

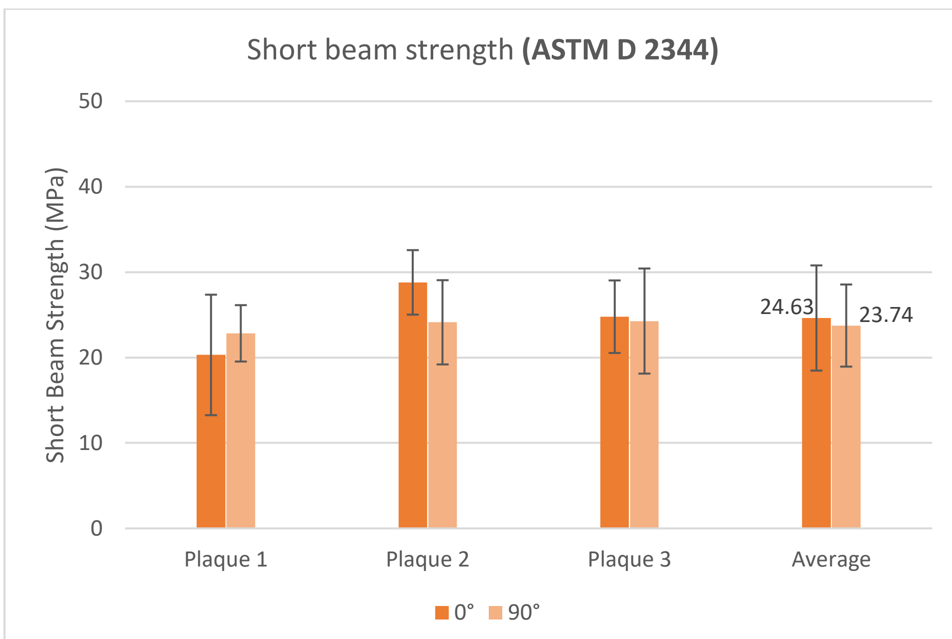


Figure 21 Shows short beam strength of the 3 co-molded plaques and their average in 0° and 90° direction

5.2.2 Inferences from the mechanical testing results:

- Improved mechanical performance
    - Comparing the strength values of co-molded plaques in Figure 18, Figure 19 and Figure 20 to the ones from LFT-D ECM, it can be clearly noticed that the addition of CR-6 organosheet material enhanced the overall mechanical performance of the LFT-D ECM material. This general trend points in a positive direction of being able to combine two materials and average the performance of the hybrid in between the two materials individually.
- Reduced the disparity between 0° and 90° direction
    - Disparity between 0° and 90° performance in the LFT-D ECM was reduced by use of the CR-6 organosheet material in the co-molded parts. This hybridized co-molded part moves away from anisotropy seen in LFT-D ECM and can be quantified as followed:
        - Tensile strength: difference in 0° and 90° decreased from 53.1% in LFT-D ECM to 36.4%
        - Flexural strength: difference in 0° and 90° decreased from 12.7% in LFT-D ECM to 7.5%
        - Izod impact strength: difference in 0° and 90° decreased from 75.5% in LFT-D ECM to 18.2%
- Short beam strength test
    - The short beam strength values showed in Figure 21 16% of the samples failed with interlaminar shear mode while 84% of the samples failed in flexure mode

6. Conclusions

Inferences from mechanical testing in section 4.2.2 and the pictures from the burn-off of LFT-D ECM samples in Figure 7 compared to the mechanical testing inferences mentioned in section 3.2.2 for AP Nylon CR-6 organosheet samples and the respective burn-off pictures in Figure 16 clearly indicate that CR-6 organosheet outperforms the LFT-D ECM material even though they both have similar matrix material and identical fiber loading by weight. Johns Manville has the ability to further enhance the fiber loading in AP Nylon CR-6 organosheet which may not be possible in LFT-D ECM process before the fiber wet-out becomes a problem. Therefore, AP Nylon CR-6 organosheet seems to be a superior material in terms of performance but an additional forming step is needed to produce the composite parts. This is why the technique of hybridization was studied by co-molding the two materials together to explore tailored locally enhanced mechanical properties in thermoplastic parts. This study was successful in terms of combining the two materials where the performance achieved was in between the two materials individually.

7. Future work

The co-molding avenue of the CR-6 organosheet with the LFT-D ECM needs to be experimented more with even more comprehensive interlaminar shear testing using methods like ASTM D5379 – shear properties testing of composite materials by the v-notched beam method (iosipescu shear). To further the co-molding capacity in addition to plaque molding for testing, some complicated part geometry molding should be performed.

8. Acknowledgement

This research was supported by Johns Manville and the we thank them for providing the raw materials needed for the research. The authors would also like to thank Dieffenbacher North America DNA and all those at the Fraunhofer Project Center for their efforts in manufacturing the materials examined in this study.

References

1. Thomason, J. and M. Vlug, *Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene: 4. Impact properties.* Composites Part A: Applied Science and Manufacturing, 1997. **28**(3): p. 277-288.
2. Hassan, A., P. Hornsby, and M. Folkes, *Structure–property relationship of injection-molded carbon fibre-reinforced polyamide 6, 6 composites: the effect of compounding routes.* Polymer testing, 2003. **22**(2): p. 185-189.
3. Karger-Kocsis, J., *Glass mat reinforced thermoplastic polypropylene*, in *Polypropylene*. 1999, Springer. p. 284-290.
4. Rohan, K., et al. *Mechanical study of direct long fiber thermoplastic carbon/polyamide 6 and its relations to processing parameters*. in *Proc. 14th-Annual SPE Automotive Composites Conference & Exhibition*. 2015.
5. Goris, S., et al., *A novel fiber length measurement technique for discontinuous fiber-reinforced composites: A comparative study with existing methods.* Polymer Composites, 2018. **39**(11): p. 4058-4070.
6. Kuhn, C., et al., *Experimental and numerical analysis of fiber matrix separation during compression molding of long fiber reinforced thermoplastics.* Journal of Composites Science, 2017. **1**(1): p. 2.
7. Ning, H., et al., *A review of Long fibre thermoplastic (LFT) composites.* International Materials Reviews, 2020. **65**(3): p. 164-188.