

# CHARACTERIZATION OF TRIBOLUMINESCENT ENHANCED GLASS FIBER COMPOSITES MANUFACTURED VIA DISPLACED FOAM DISPERSION TECHNIQUE

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## ABSTRACT

This paper discusses the manufacture and characterization of triboluminescent (TL) multifunctional composites made via the novel displaced foam dispersion (DFD) technique. TL crystals are encapsulated in polystyrene (PS) foams in 0, 2, 4 and 50wt% loadings. The PS-TL foams are integrated into glass fiber laminates and the shear properties are observed. It was found that the introduction of PS foam into glass fiber laminates decreased the shear properties. However, the integration of PS-TL foams leads to an increase in shear properties when compared to glass fiber specimens containing only PS foams.

## 1 INTRODUCTION

Since the launch of the Boeing 787, more is being required of composite structures. For example, there has been an abundance of research interest in the incorporation of various particulates such as carbon nano tubes (CNT's), nano clay, carbon nano fibers, silica, etc. into composite structures. There has also been great interest in adding layers to composite structures such as bucky paper interleaves, SMART layers®, piezoelectric thin films waivers, optical fibers, etc.

The overall goal is the enrichment of mechanical properties of composites such as high strength, stiffness, fracture toughness and damping as well as the implementation of intrinsic functional properties into composites such as electrical conductivity, self-healing, and thermal insulation, power saving, *in situ* monitoring or self-monitoring. This pursuit of mechanical as well as functional properties in composite laminate structures has given rise to the term *multifunctional fiber reinforced composites* [1].

The manufacturing of multifunctional fiber reinforced composites typically involves the integration of functional components during traditional composite fabrication processes such as vacuum assisted resin transfer molding (VARTM), resin film infusion (RFI) and resin transfer molding (RTM). However, the integration of functional components is often plagued with difficulties. CNT's for example, are difficult to disperse into liquid resin and prevent resin flow because CNT's are filtered by fibers upon resin infusion [2, 3]. Larger components such as thin films or layers also obstruct resin flow, along with some added concerns regarding composite delamination [4].

Displaced foam dispersion (DFD) is proposed as a novel technique used for the easy integration of functional components into fiber reinforced composites (FRC's) (Figure 1). The functional components are first integrated into an expendable polystyrene (PS) foam. The augmented foams are then sandwiched between composite fiber layers. Upon infusion, the resin matrix depletes or melts the polymer foam, leaving the functional components *in-place* [5].

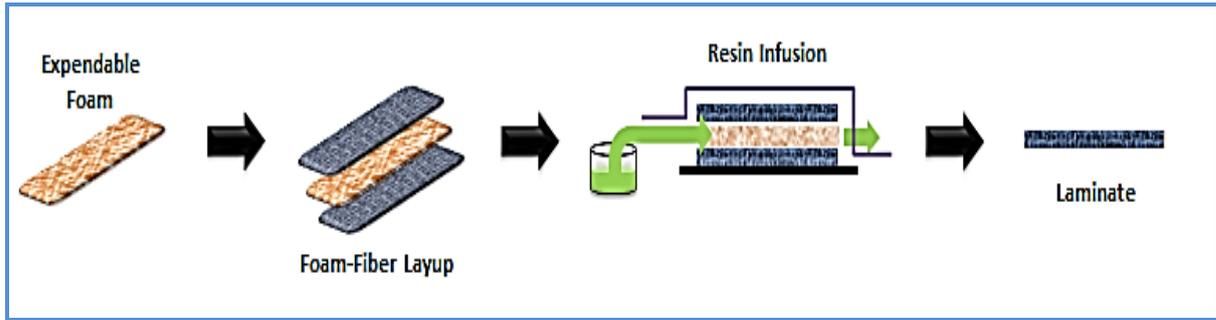


Figure 1: Displaced foam dispersion technique.

Suitable functional components for which the DFD technique can be prescribed are TL crystals. Their inherent ability to emit light when broken or stressed makes them ideal candidates for the global and *in situ* monitoring of FRC's [6, 7]. Unfortunately, TL crystals are very dense and tend to sediment or 'sink' in liquid resin during composite manufacturing. This results in poor crystal dispersion and a subsequent reduction in mechanical properties.

There has been little work aimed at the tactful integration of these particles into composite laminates for structural and functional performance. Frketic et al. [8] investigated the impact resistance of triboluminescent-enhanced composites by integrating TL crystal in glass fiber composites by way of TL crystal doped resin plates and found a good correlation between impact force and damage. Dickens et al. [9] reported on the tensile properties of TL crystal doped laminates. In this case, TL crystals are dispersed by using a rotational vacuum infusion apparatus. It was found that the increase of TL crystals concentrations lead to a reduction in laminate tensile strength.

This work seeks to utilize the novel DFD technique for the integration of TL crystals into glass fiber laminates and observe the mechanical behavior particularly short-beam shear properties. First, the TL crystals are dispersed into glass fiber composites via the DFD technique. Finally, TL foams are put into laminates and tested for shear properties.

## 2 MATERIALS AND METHODS

### 2.1 Fabrication of TL Foams

The polystyrene pellets used for foaming are purchased from Entec Polymers in Orlando, FL. There are two high intensity TL crystal types used in this study. Manganese-doped zinc sulfide (ZnS:Mn) has the highest TL emissions for inorganic crystal types provided by Phosphor Technology (UK) having a material density of  $4.1\text{kgm}^{-3}$  [10]. The europium dibenzoylmethide triethylammonium (EuD4TEA) or europium crystals doped with dimethyl methylphosphonate (DMMP) have the highest TL intensity for organic crystals and are made in-house [11]. The encapsulation of TL crystals into PS foam is a three stage process (Figure 2).

In stage 1, PS pellets are dissolved at  $90^{\circ}\text{C}$  in dimethylformamide (DMF) solvent followed by the addition of TL crystals. The DMF-PS-TL crystal solution is then allowed to cool down and is added dropwise into a shear mixer containing de-ionized (DI) water. The volume ratio of DMF:DI-water is 1:5. The solution is then filtered and dried into a TL raw material powder (TL-RM).

In stage 2, the TL-RM powder is re-dissolved in 50ml of DMF, followed by the addition of 5wt% 2,2'-Azobis(2-methylpropionitrile) (AIBN) (foaming agent). The solution is left spinning for 6-24hrs. During this time period, the PS solidifies upon cooling and traps the suspended crystals between the polymer chains thus preventing crystal sedimentation. This is also meant to ensure good distribution of TL crystals within the PS matrix and thereby the final composite. The end result is a malleable 'taffy'

like ball [12]. The taffy is then soaked in acetone for 24hrs in order to allow for low temperature foaming.

Finally, in stage 3, the taffy is compressed at a low temperature of 70°C. During these heating and pressing processes, the AIBN decomposes and releases nitrogen gas resulting in a porous foam structure. Stages 1-3 are repeated until 0, 2, 4 and 50wt% TL foams are produced. These weight percentages were chosen to capture the effects of high and low crystal loadings. For the purpose of short hand, Table 1 is a description of the composite specimens produced. It illustrates the crystal weight percentages in foams and constituents in the composite.

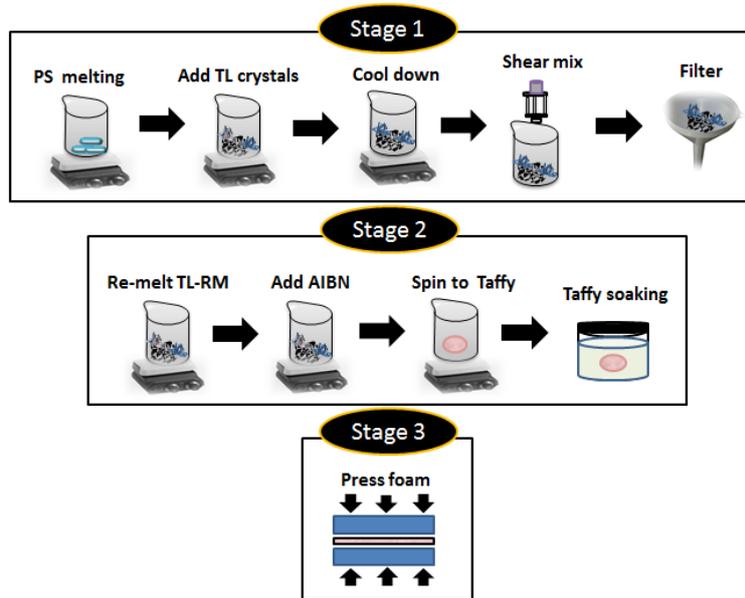


Figure 2: Three stage PS-TL foam fabrication process.

Table 1: Composite specimen description via constituents and crystal type

Sample Nomenclature	Crystal Type	Crystal Loading in Foam (wt%)	Composite Description
Neat	N/A	0	Glass fiber composites with no foam or crystals
Neat-PS		Glass fiber composites containing only PS foam and no crystals	
2wt-crystal type	ZnS:Mn or Europium	2	Glass fiber composites with 2wt% loading of crystals in PS foam
4wt-crystal type		4	Glass fiber composites with 4wt% loading of crystals in PS foam
50wt-crystal type		50	Glass fiber composites with 50wt% loading of crystals in PS foam

## 2.2 TL Composite Fabrication and Mechanical Testing

The reinforcements utilized are 2D woven glass fabrics. Armorstar IVEXC410 vinyl ester resin from Cook Composites & Polymer (CCP) and methyl-ether ketone (MEKP) from Norac Inc. are used. The TL-foams are then placed in-between glass fiber fabric and infused with vinyl ester resin. Figure 3a depicts the TL composite after VARTM fabrication. After resin curing, the subsequent TL laminates are cut via a water-cooled diamond saw into rectangular bars and sanded into shape. Overall, there are three layers of glass fiber and two foam layers used to manufacture each 2mm short-beam shear specimen.

The TL composites are tested in accordance with the ASTM D2344 standard for short-beam strength of polymer matrix composite materials and their laminates. A table top MTS insight mechanical tester in combination with a 1kN load cell was used to apply and monitor force and resulting displacement on/of the specimens. A span to depth ratio of 4 was chosen so as to permit shear failure. Figures 3b & 3c illustrate specimens with and without TL crystals under ultraviolet (UV) light before testing, respectively. The yellow-orange of the specimens result from TL crystal photoluminescence. This confirms the presence of the TL crystals in the composite and is also an early indication of some crystal dispersion within the composite.

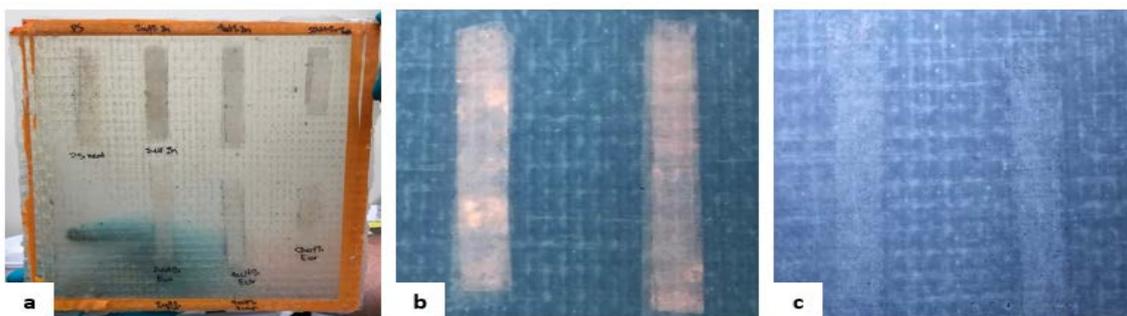


Figure 3: Triboluminescent composite a) after VARTM processing, b) specimens with ZnS:Mn crystals under UV light and c) specimens without crystals under UV light.

## 3 RESULTS AND DISCUSSION

### 3.1 Mechanical Characterization

The short-beam strength of TL composites is shown in Figure 4. There is a 44.10%, 40.10%, 44.09% and 28.29% overall decrease in short-beam strength for TL composites containing Neat-PS foam, 2wt-ZnS:Mn, 4wt-ZnS:Mn and 50wt-ZnS:Mn foam respectively as compared to the Neat reference specimen (Figure 4a). Likewise, there is a 44.10%, 35.17%, 28.41%, 18.32% decrease in short-beam strength for TL composites containing Neat-PS foam, 2wt-europium, 4wt-europium and 50wt-europium foams respectively as compared to the Neat reference specimen (Figure 4b).

Should a line be drawn through the error bars of both Figure 4a and Figure 4b bar graphs, there is not a large difference to be seen in short beam strength due to the variation in the data sets between the two crystal types. In examining this, the possible difference could be due to the characteristics of the crystals and their interaction with vinyl ester resin. The inorganic ZnS:Mn crystals are smaller and harder in nature when compared to the larger and softer europium crystals. Yet, the europium specimens outperformed the ZnS:Mn specimens. This may be owed to the differences in miscibility of both crystal types with vinyl ester resin. For example, in the case of thermosets toughened by rubber particles, the crosslinking of the thermoset within the rubber phase generates a high strength fibril formation that toughens the rubber and averts rubber particle fracture [13]. Similarly, the europium

crystals and vinyl ester may interact more favorably during crosslinking than ZnS:Mn particles.

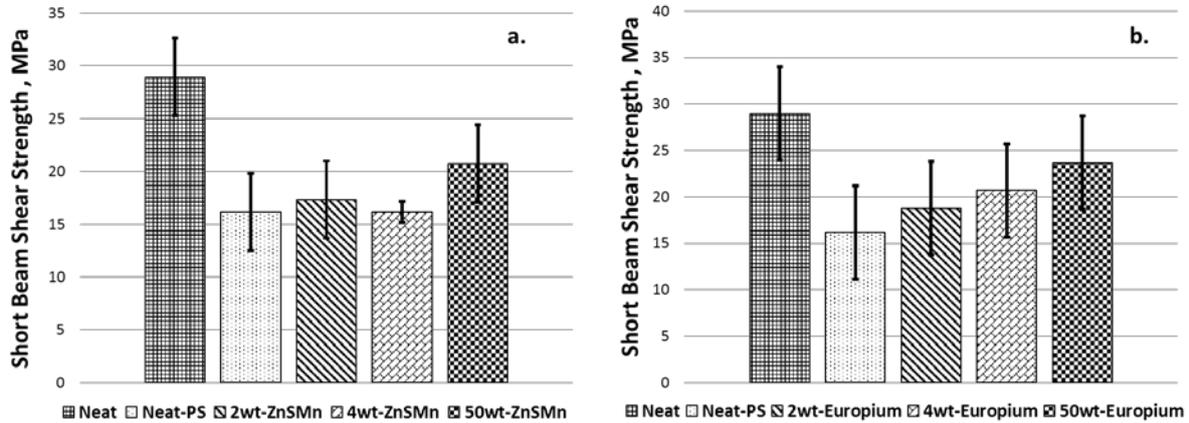


Figure 4: Shear properties of TL composites a) ZnS:Mn specimens and b) europium specimens.

The decrease in short-beam strength when comparing the Neat specimen to the Neat-PS (i.e. the addition of just PS foam, no crystals) could also be due to the blended nature of the PS foam which is a thermoplastic polymer and vinyl ester resin, a thermoset polymer. When blending thermoplastic and thermoset polymers, it is not uncommon to observe instances of phase separation. In fact, there are a variety of factors that can induce phase separation including higher degrees of thermoplastic loadings in the thermoset in polymer blends and weak interaction forces between the blended components [14]. Vinyl ester resin and PS are known to be miscible polymers [15]. This suggests that the molecular interaction between them when blended should be strong enough to resist phase separation. In addition to this, the PS is in a foamed state meaning that it is associated with low densities and corresponding mass. As such, the loadings of PS in vinyl ester may not be high enough to cause phase separation.

Another possibility is a type of phase separation due to the concurrent dissolution of the PS foam and curing of the vinyl ester resin. This phenomenon is called ‘incomplete phase separation’ and occurs when there are a variety of chemical reactions occurring simultaneously in the blended system during curing [16]. In this case, the curing reaction reaches completion before the other reactions in the system reach completion, freezing the system in a non-equilibrium state. This may be the more likely case as the dissolution of polymers without temperature is known to be a ‘slow moving’ endothermic reaction that requires time for the solvent molecules to separate and bind to the solute molecules [17]. Therefore, it is likely that PS molecules bind to the vinyl ester molecules through dissolution slower than the crosslinking rate of the vinyl ester molecules. This results in incomplete phase separation and a subsequent reduction of composite strength properties when comparing the Neat and Neat-PS specimens.

Moreover, it was expected that there would be a decrease in strength with the increasing addition of crystal loadings to the foam in the glass fiber composite. For instance, the addition of the TL crystals to the PS foam increases the short-beam strength by 28.29%, 15.97%, 28.07% and 46.12% for 50wt-ZnS:Mn, 2wt-europium, 4wt-europium and 50wt-europium specimens respectively when compared to Neat-PS foam specimens. While the interaction between the TL crystal-PS foam and the remaining composite constituents could have aided in some way to the absorption of the load, more investigation is clearly needed to define the mechanics of this phenomenon. It was also expected that there would be a significant change in short-beam strength and modulus between 2wt% and 50wt% foam specimens for each crystal type due to the increase/differences in TL loading.

## 4 CONCLUSIONS

Two types of triboluminescent multifunctional composites are fabricated by way of the novel displaced foam dispersion technique. The short-beam shear strength of triboluminescent composites are also investigated. There is an overall decrease in short-beam shear strength when TL foams are added. Specifically, there is a decrease (i.e. 44.10%) in short-beam shear strength with the addition of polystyrene foam (i.e. Neat-PS specimens) but an increase when triboluminescent crystals are added to the foam as compared to only the polystyrene foam specimens. This was said to be due to the competing and simultaneous dissolution of the polystyrene foam and crosslinking of the vinyl ester resin.

Over all, the observations made revealed points of interest for future study. Future work will involve studies to understand and optimize the kinetics of vinyl ester resin, PS foam and TL crystal relations for the overall enhancement of glass fiber composite properties. For instance, should the Neat-PS composite case be optimized through changes in fiber layup, resin-foam kinetics and changes to foam morphologies, will the addition of TL crystals greatly improve glass fiber composite properties? In addition to this, triboluminescent composites will be evaluated under a broad spectrum of loading conditions such as tensile, flexural and impact loading to create a performance index for these materials and their potential use in the *in-situ* monitoring of fiber reinforced composites.

## REFERENCES

- [1] Gibson, R.F., *A review of recent research on mechanics of multifunctional composite materials and structures*. Composite Structures, 2010. **92**(12): p. 2793-2810.
- [2] Kim, M., *Processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites*. Composites Science and Technology, 2009. **69**(3-4): p. 335-342.
- [3] McCrary-Dennis, M.C.L. and O.I. Okoli, *A review of multiscale composite manufacturing and challenges*. Journal of Reinforced Plastics and Composites, 2012. **31**(24): p. 1687-1711.
- [4] Abot, J.L., et al., *Delamination detection with carbon nanotube thread in self-sensing composite materials*. Composites Science and Technology, 2010. **70**(7): p. 1113-1119.
- [5] Okoli, O.O. and M. Kim, *Composite Materials and Methods for Selective Placement of Nano-Particulates within Composites*. 2013, Google Patents.
- [6] Olawale, D.O., et al., *Triboluminescence multifunctional cementitious composites with in-situ damage sensing capability*, in *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2012, Pts 1 and 2*, M. Tomizuka, C.B. Yun, and J.P. Lynch, Editors. 2012.
- [7] Olawale, D.O., et al., *Mimicking the Human Nervous System with a Triboluminescence Sensory Receptor for the Structural Health Monitoring of Composite Structures*, in *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2011*, M. Tomizuka, et al., Editors. 2011.
- [8] Frketic, J., et al., *Measurement of impact force for triboluminescent-enhanced composites by modified impulse method*. Journal of Reinforced Plastics and Composites, 2016. **35**(11): p. 915-923.
- [9] Dickens, T.J. and O.I. Okoli, *Enabling damage detection: manufacturing composite laminates doped with dispersed triboluminescent materials*. Journal of Reinforced Plastics and Composites, 2011. **30**(22): p. 1869-1876.
- [10] Xu, C., et al., *Preparation and characteristics of highly triboluminescent ZnS film*. Materials research bulletin, 1999. **34**(10): p. 1491-1500.

- [11] Fontenot, R.S., et al., *Synthesis and characterization of highly triboluminescent doped europium tetrakis compounds*. Journal of Luminescence, 2012. **132**(7): p. 1812-1818.
- [12] McCrary-Dennis, M., M.J. Uddin, and O.I. Okoli, *Synthesis and characterization of polystyrene carbon nanotube nanocomposite for utilization in the displaced foam dispersion methodology*. Composites Part B: Engineering, 2016. **98**: p. 484-495.
- [13] Walker, I. and A. Collyer, *Rubber toughening mechanisms in polymeric materials*, in *Rubber toughened engineering plastics*. 1994, Springer. p. 29-56.
- [14] Hwang, J., et al., *Effects of molecular weight of polysulfone on phase separation behavior for cyanate ester/polysulfone blends*. Journal of applied polymer science, 2000. **77**(4): p. 921-927.
- [15] Varma, I., et al., *Effect of styrene on properties of vinyl ester resins, I*. Macromolecular Materials and Engineering, 1985. **130**(1): p. 191-199.
- [16] Eitouni, H.B. and N.P. Balsara, *Thermodynamics of polymer blends*, in *Physical Properties of Polymers Handbook*. 2007, Springer. p. 339-356.
- [17] Miller-Chou, B.A. and J.L. Koenig, *A review of polymer dissolution*. Progress in Polymer Science, 2003. **28**(8): p. 1223-1270.