

ASSESSMENT OF EFFECTS OF ALUMINA NANOFIBERS ON WETTABILITY, VISCOSITY, AND MECHANICAL PROPERTIES OF UNSATURATED POLYESTER

Harish S. P. Kallagunta^{1,2}, Subash Panta², Aziza Nahar², and Jitendra S. Tate^{1,2,*}

Texas State University

601 University Drive, San Marcos, TX, 78666

¹Materials Science Engineering and Commercialization Program, Texas State University

²Ingram School of Engineering, Texas State University

JT31@txstate.edu; 512-245-1826

ABSTRACT

Increase in viscosity, poor wettability and agglomeration are the major issues when using nanoparticles to enhance the properties of polymeric materials. Processability of composites becomes challenging with the increase in the viscosity. A study has been made on the effects of alumina nanofiber modification on the viscosity and mechanical strength of unsaturated polyester resin. Additionally, wettability studies of the alumina nanofiber with unsaturated polyester resin using contact angle measurements were compared. Tension, Flexure and Izod impact tests were performed on 0.25wt%, 0.5wt%, 0.75wt% and 1wt% loading levels of alumina nanofibers in unsaturated polyester matrix and were compared to neat composites. Alumina nanofibers were dispersed in unsaturated polyester resin using three roll mills. Nanomodified and neat polyester coupons were cast in silicon molds according to the standards. TEM Images revealed good dispersion. Silane treatment proved to improve the homogeneity in dispersion and positively affect the viscosity. In terms of mechanical properties, silane treatment proved to be effective at lower loading levels. However, at higher loading levels, silane treatment was outperformed by untreated alumina nanofibers.

1. INTRODUCTION

Due to the covalently bonded network with high crosslinking density and localized plastic deformation in front of the crack-tip under mechanical loading leads to catastrophic failure in thermoset resins. Polyester resin among the thermoset resins have highest applications in the industry despite their low mechanical properties, due to their affordability and ease of processing. Nanoparticle modification of polymeric materials has gained prominence in the recent decade in the development of composite materials to make them multifunctional. Nanoparticles are more

Copyright 2020. Used by the Society of the Advancement of Material and Process Engineering with permission.

SAMPE Virtual Conference Proceedings, 2020. Society for the Advancement of Material and Process Engineering – North America.

effective because of the high surface area to volume ratio. Hence very low filler content is required to achieve desired properties. However, the incorporation nanoparticles into the polymer matrix is challenging because of complications such as increase in viscosity, agglomeration and poor exfoliation [1-3].

Diverse varieties of nanoparticles are studied to enhance the performance of the unsaturated polyester resin. Carbon nanotubes[4-6], Nanosilica[7, 8], Fumed silica [9-11], nanoclay [12], halloysite nanotubes[13, 14] and elastomers[15] modification of unsaturated polyester is studied by various researchers in understanding its effect on the static, dynamic, thermal and electrical properties. Yu et al [16]studied graphene oxide as the coupling agent for graphene nanoplatelets/epoxy composites and found improvement in toughness by 110% at 0.86wt% loading. Lavoratti et al[17] has studied the effects of methoxy and ethoxy silane on the graphene nanoplatelets. The study has shown improvement in tensile strength by 21.7% and glass transition varied by 8% at 0.25wt% loading level of (3-glycidyloxypropyl) Trimethoxy silane treated graphene nanoplatelets. Tee et al [18], has demonstrated that the silane treated silver nanoparticles in epoxy composites further enhances the multifunctionality of the composites. The silane treatment has also proven effective to increase dispersibility of silver nanoparticles. Fracture toughness K_{IC} and G_{IC} improvement with the use of silane functionalization of graphene oxide for epoxy composites by 39% and 83% is observed in studies by Wan et al[19]. Improvement in thermal stability at 0.5wt% and improvement of tensile, flexure properties with silane functionalization was observed. Amide and imide based functionalization of silica nanoparticles for polyester nanocomposites is studied by Ghosh et al and the group observed increased thermal stability in the nanocomposites[20]. Alumina nanofibers, which are relatively new form of nanomaterials, are studied on their effectiveness in strengthening the polymer matrix for fiber reinforced composite materials. Mechanical, thermal stability and flammability characteristics of PA6 thermoplastics modified with alumina nanofibers by Wu et al [21] reported a significant effect of alumina nanofiber modification on the mechanical properties although there is no change in thermal and flammability properties. Raikitin and Grodensky [22], reported an increase in mechanical property by 72% by adding alumina nanofibers to the epoxy resin.

This research study is aimed at understanding the effects of alumina nanofibers on the physical, morphological and mechanical properties when incorporated into the polyester matrix. The effect

of surface treatment on the alumina nanofibers on the above properties at four different loading levels was compared with the untreated alumina nanofibers modified polyester.

2. MATERIALS AND MANUFACTURING

2.1 Material System:

The material system used for this study comprises of unsaturated polyester resin SIL47DA-2949 with a viscosity of 396 cP from Interplastic Corporation. Alumina nanofibers with minimal aspect ratio 18-20 under trade name NafenTM from ANF technologies were used as nanofillers. Benzoyl Peroxide was used as the curing agent with heat as an external stimulator. One set of polymer samples are modified with untreated alumina nanofibers and the second set were modified with vinyl silane coupling agent treated alumina nanofibers. Loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% were used for both polymers.

2.2 Sample fabrication

2.2.1 Dispersion using calendaring approach

Three-roll milling was used for dispersing NafenTM into the polyester resin. In every pass, by adjusting the gap setting between the rollers a high shear force was achieved to reduce the clumps and clusters formed. The gap between the rollers was set at 25 μ m, 15 μ m, and 7.5 μ m respectively for three passes. Vinyl silane coupling agent treated alumina nanofibers were also dispersed using the same approach.



Figure 1: Three roll mill and illustration of dispersion using calendaring approach (Courtesy: www.exaktusa.com)

2.2.2 Fabrication of polymer test coupons

The untreated alumina nanofiber (UT-ANF) modified polyester resin and vinyl silane treated alumina nanofiber (VT-ANF) modified polyester resin were cast into silicon molds made as per the ASTM standards and were cured in the oven at 80C as per the specifications of personnel at

Interplastic corporation. The cured modified polyester coupons were then post-cured for three hours at 110 °C in the programmable oven.

3. EXPERIMENTATION

3.1 TEM Imaging

In order to evaluate the dispersion state of alumina nanofibers in the polyester, Transmission Electron Microscopy was performed on the polymer coupons. Copper grids were used on which thin sections of polymer modified with alumina nanofiber obtained using ultra microtome are placed. The grids were then viewed in a high-resolution transmission electron microscope.

3.2 Refractive Index

The refractive index measurements were calculated using Bausch & Lomb Abbe-3L Refractometer. The sample is then carefully placed on the prism to form a thin film across the whole prism and the prism was closed. Adjusting the lamp so the light shines on the prism and looking through the eyepiece, the index of refraction is recorded.

3.3 Viscosity

The effects of adding UT-ANF and VT-ANF on the viscosity of the unsaturated polyester resin were studied using the Thermo Scientific Haake Viscotester. Along with the effects of surface treatment, the loading weight percentage of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% were also studied and reported as compared to viscosity of neat unsaturated polyester resin. 15mL of the sample was placed inside the immersion tube and a rotor (coaxial cylinder) was used to measure the shear rate and viscosity. All the samples are tested at room temperature. The shear rate vs shear stress plots were graphed, and viscosity is measured as the slope of the curve.

3.4 Wettability

Rame-hart contact angle goniometer is used to measure the contact angle to get an understanding of the wettability. The UT-ANF and VT-ANF modified polyester resin droplets are carefully dropped on to the GPC substrate and with the aid of a telescopic eyepiece the angle of the resin on the substrate is measured.

3.5 Mechanical testing

The static testing on the untreated and vinyl treated Alumina nanofiber (ANF) modified polyester coupons is performed using UTS electromechanical system. Tensile, Flexure and Izod impact tests performed on the polyester coupons (UPE) modified with untreated and surface treated

Alumina nanofibers (ANF). The tensile tests were conducted according to ASTM D638 at a loading rate of 1mm/min. The ultimate tensile strength (UTS), modulus and percentage elongation were obtained from this test. Flexure testing was conducted according to the ASTM D790 standard at a loading rate of 0.10mm/min. Izod impact testing was done according to the ASTM D256 standard and were subjected to a constant energy of 9J, to obtain the impact strength of the polymer coupons.

4. RESULTS AND DISCUSSION

4.1 TEM Analysis

The TEM images as shown in Fig 2, revealed agglomeration of ANF nanoparticles in UPE at higher loading levels, whereas a decent quality of dispersion of ANF nanoparticles in lower loadings is observed. It was observed that ANF nanoparticles are retaining their fiber like morphology even after subjecting to high shear forces via three roll milling. Although individual ANF nanoparticles are visible, it is observed that the fibers are not completely de-bundled and distributed. The lack of de-bundling might be because of absence of any surface treatment. It would be interesting to see the effect of surface treatment of ANF on the de-bundling and distribution aspect of the nanoparticles during dispersion.

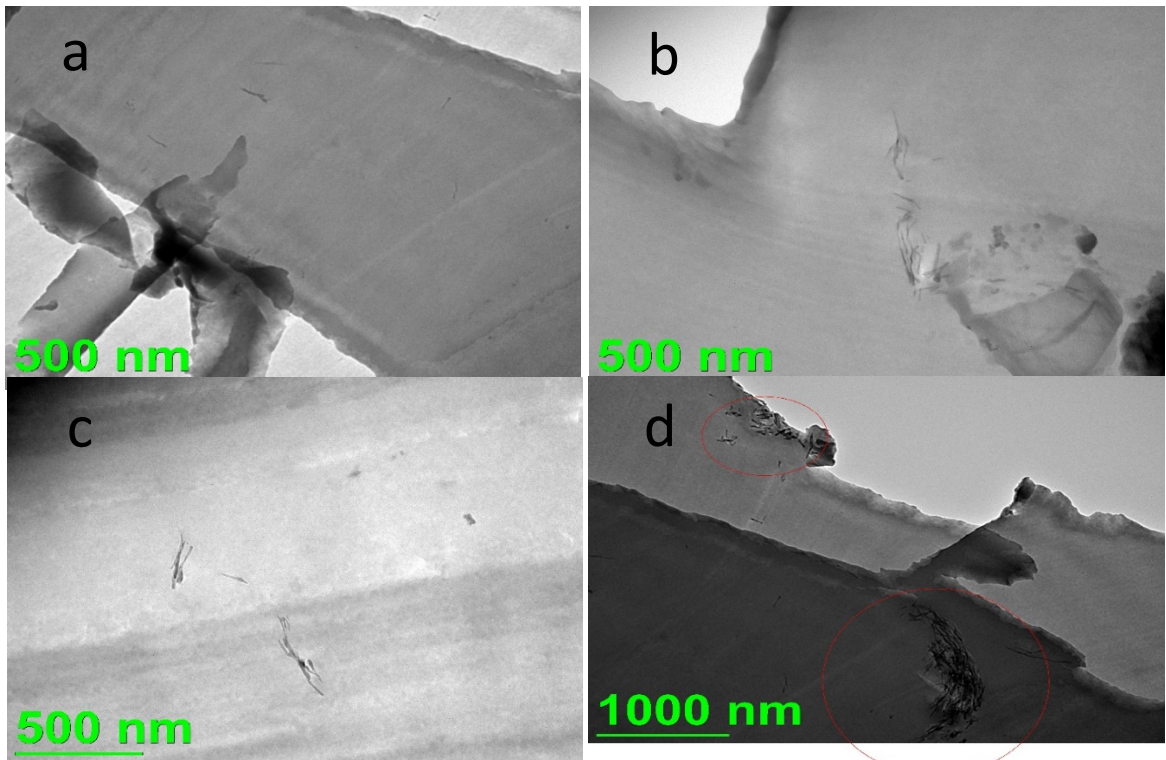


Figure 2: TEM images showing dispersion of Untreated ANF in UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

4.2 Refractive index

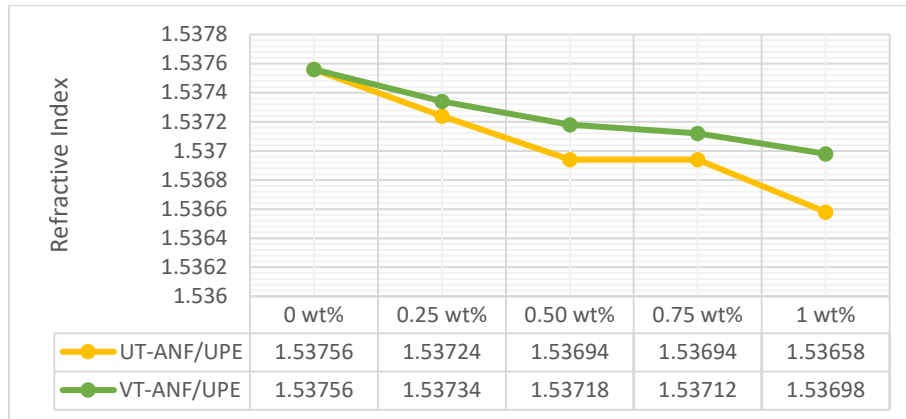


Figure 3: A summary of comparison of refractive index of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

The refractive index measurement is ratio of velocity of light in vacuum to the velocity of light in the polyester resin medium. The refractive index values showed consistency for respective loading wt% as shown in Fig 3. The VT-ANF/UPE as compared to UT-ANF/UPE showed good refractive index values meaning that the silane treatment of alumina nanofibers provided a good measure for homogenous dispersion. The refractive index values as compared to the control are very less indicating the presence of alumina nanofibers, the decrease in the values with increased loading wt% is due to the light encountering alumina nanofibers and deflecting the light reducing the index of refraction.

4.3 Viscosity

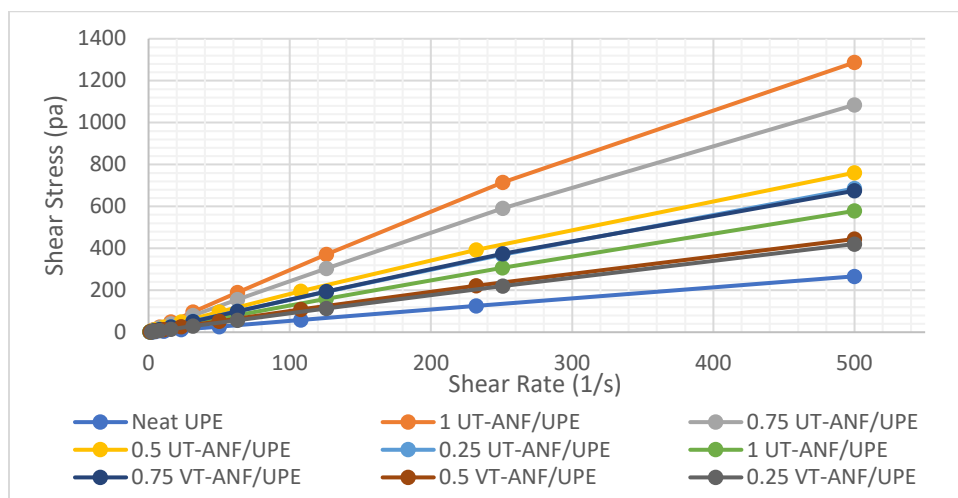


Figure 4: A summary of viscosity change of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

Table 1: Viscosity values of UT-ANF/UPE and VT-ANF/UPE

Loading wt%	Viscosity (cP)	
	UT-ANF/UPE	VT-ANF/UPE
0.00	534.3	
0.25	1380.6	844.2
0.50	1528.8	890.9
0.75	2186.9	1364.0
1.00	2601.0	1162.3

The shear rate vs shear stress plots are given in figure 4. The graphs of shear stress vs shear rate showed a linear relation, which means the non-modified resin, shows a Newtonian behavior. A look at the plots gives the understanding of change in viscosity with increase in the loading wt% of alumina nanofibers in the polyester. The surface treatment of alumina nanofibers helped in reducing the viscosity of the polyester resin with respect to the as received alumina nanofiber modified polyester. It is evident from this plot that with surface modification, the viscosity of nanomodified polyester can be achieved and thus processing challenges can be addressed. Table 1 gives an understanding of the viscosity changes with addition of nanoparticles and the effect of surface treatment on the viscosity property. It is quite evident that, surface treatment of alumina nanofibers has a positive effect on the change in viscosity. The addition of surface functional groups reduces the attraction among the nanoparticles thus increasing homogenous dispersion. For affordable processes such as vacuum assisted resin transfer molding (VARTM) or layup, the ideal viscosity range is 100-3000cP. When using vacuum assisted resin transfer molding, high viscosity of the resin poses a challenge of increased time of resin infusion thus increasing the fabrication time. In case of hand layup, high viscosity of the resin increases the air pockets during the wetting of the fabrics. From the above result, a surface treatment of the nanoparticles can help reduce the processing challenges associated with high viscosity.

4.4 Wettability

The degree to which liquids wet a fiber is a measure of the bonding between the fiber and the resin, which results in efficient stress transfer between matrix and reinforcement. The contact angles measured provide information about wettability, essential in selecting or adjusting the modifications on nanomaterial or fiber surfaces. The nanoparticle modification of polyester resin changes the variation of the surface energy of the resin droplets when added to the substrate thus varying the wettability of the glass fibers. Surface treated alumina nanofibers during the dispersion

process broke down into smaller nanofibers providing continuous surface reducing the surface energy and thus increasing the wettability. The agglomerated lumps during the higher concentration levels, creates a continuous rough surface thus by increasing the wetting angle. However, the results in this study suggest there is not big influence in loading percentage of alumina nanofiber except for the silane modification.

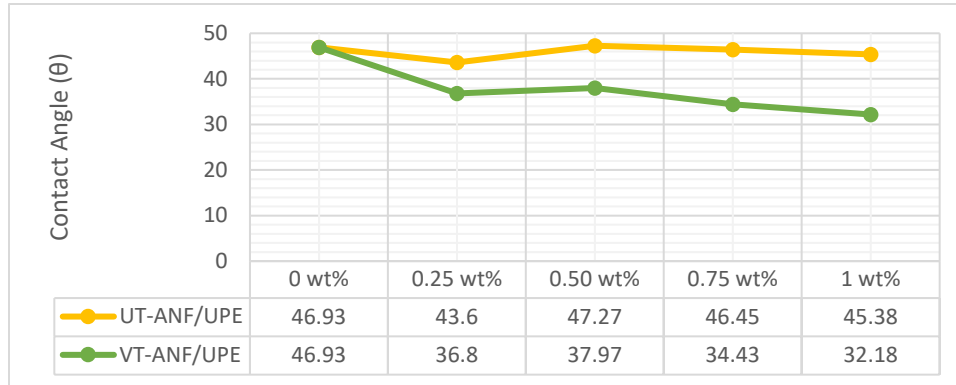


Figure 5: A summary of contact angle measurements of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

4.5 Mechanical properties

Tensile Properties

As observed in Fig 6, no significant improvement in the tensile strength of the ANF/UPE was observed, although an increase of tensile modulus at 0.25wt% loading level is observed. The tensile properties when used with both UT-ANF and VT-ANF, initially declined, but regained at a loading of 1wt%. The tensile strength of the VT-ANF/UPE as compared to the UT-ANF/UPE is a result of the homogenous dispersion, which is facilitated through the surface treatment. The tensile modulus of UT-ANF/UPE is high as compared to the VT-ANF/UPE. Equilibrium toughness as shown in Fig 7, has seen a consistent improvement with silane treated alumina nanofiber modified polyester coupons. This behavior shows that, the surface treatment enhanced the bonding between the matrix and nanofiber, thus increasing the work done on the sample. The three-roll mill process induces high shearing forces as the distance between the rollers is decreased, which possibly dealt with efficient de-bundling of alumina nanofibers during each pass. However, it was observed from TEM images at higher loading levels, the alumina nanofibers tend to agglomerate which is possibly due to the high surface areas of nanofibers, meaning that even the aspect ratio is maintained, they tend to act as stress concentrators.

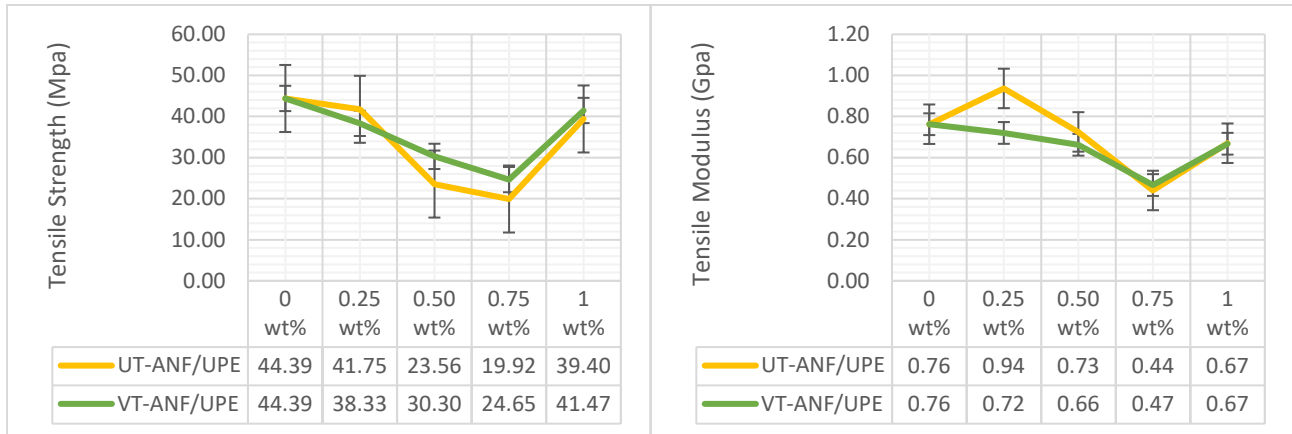


Figure 6: Tensile strength and tensile modulus comparison of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

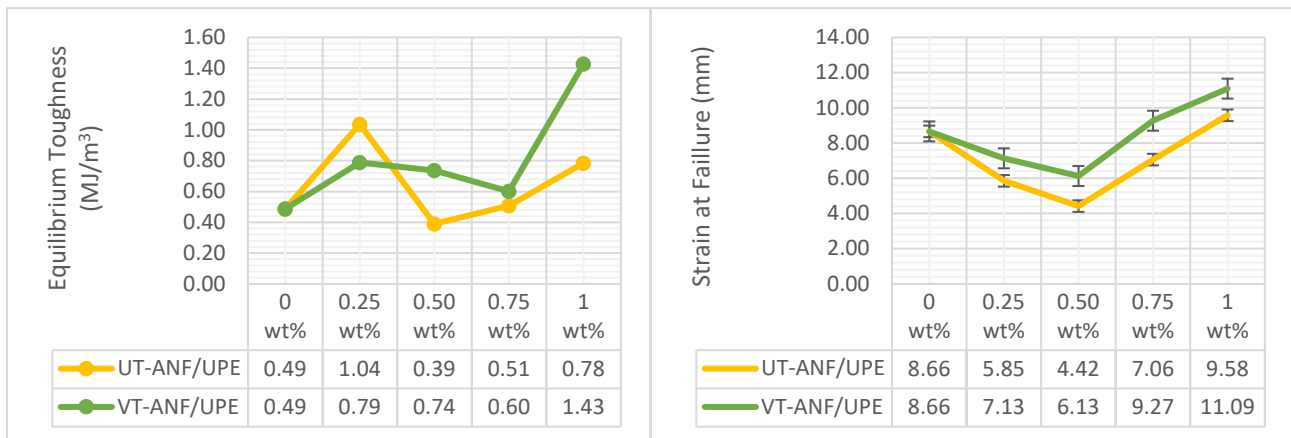


Figure 7: Equilibrium toughness and strain at failure of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

Flexure Properties

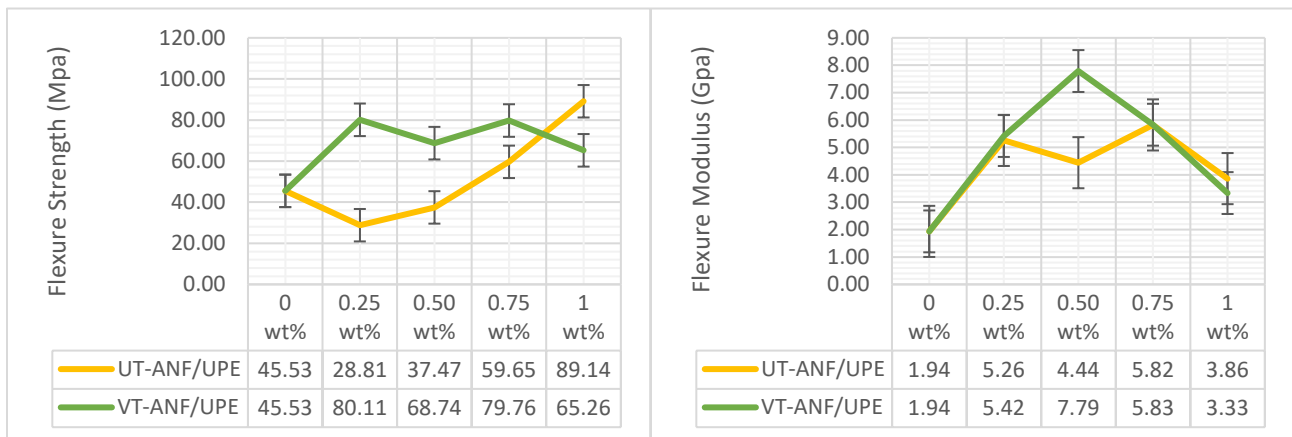


Figure 8: A summary of flexure properties of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

The flexure properties as shown in fig 8, shows the effect of nanoparticles in the polyester resin. Due to the unique fiber like morphology, the alumina nanofibers could deflect the force, thus causing an increase in the properties. The silane treatment of the alumina nanofibers has proven to be effective in increasing in the flexural strength and flexural modulus of the polyester resin coupons. The as received alumina nanofibers modified polyester composites initially has seen a decrease in their strength values but regained their performance after 0.50wt%. It is well known that increase in flexure strength and flexure modulus would result in higher toughness values, which is a result of the difficulty of crack initiation and propagation within matrix.

Izod Impact

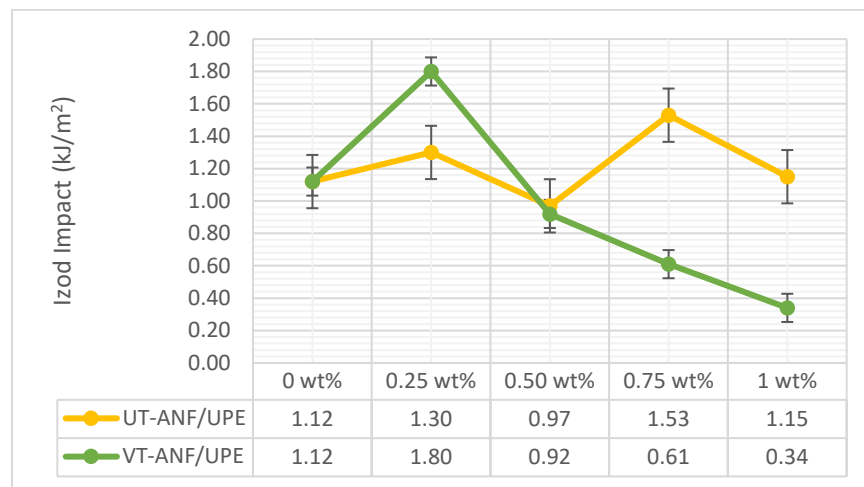


Figure 9: A summary of Izod impact of UT-ANF/UPE and VT-ANF/UPE at loading levels of (a) 0.25wt%, (b) 0.5wt%, (c) 0.75wt% and (d) 1wt%

The Izod impact strength of the nanomodified polyester coupons is reported in fig 9. The impact results show a dependence of the loading percentage on the impact energy absorbed by the polymer coupons. The VT-ANF/UPE initially has seen an increase in the energy absorbed at 0.25wt%, but further the energy absorbed drastically decreased. The UT-ANF/UPE has seen mixed results. At 0.25wt% loading level of VT-ANF/UPE the impact toughness of the polymer increased by 60% and the impact strength of UT-ANF/UPE polymer composite is increased by 36.6%.

CONCLUSION

Transmission electron microscopy, viscosity, wettability, refractive index, tensile, flexure and Izod impact property of polyester coupons modified with untreated as received alumina nanofibers and silane treated alumina nanofibers is studied and compared. TEM Images showed agglomeration but decent dispersion at higher loading levels. As expected, viscosity increased with loading level

of alumina nanofibers. Silane treatment has proven effective to impart mechanical properties at reduced viscosity. The refractive index also proves the efficiency of silane treatment of alumina nanofibers in promoting homogenous dispersion into polyester resin.

1. The viscosity rise observed was not substantial in polyester modified with silane treated alumina nanofibers. At 0.25wt% loading level, the viscosity rises in VT-ANF/UPE was only 58% as opposed to 158% at same loading level of UT-ANF in polyester.
2. Regardless of the silane treatment of alumina nanofibers, major of the mechanical properties showed good improvement at 0.25wt% loading level.
3. The equilibrium toughness, which is an important parameter against deformation, has seen an improvement of 112.2% at 0.25wt% loading level of UT-ANF in polyester. With silane treatment at 1wt% loading level has seen a maximum improvement of 191.8%. The silane treatment of alumina nanofibers.
4. Flexural properties have improved with addition of alumina nanofibers. However, with silane treatment it was observed that 0.25wt% loading level the strength improved by 43.3%.
5. Izod impact property of the polyester modified with VT-ANF at 0.25wt% loading level has seen maximum improvement by 60.7%.
6. It can be concluded from this study that the inclusion of alumina nanofibers has shown high potential of improving the mechanical properties. It is validated that surface treatment of alumina nanofibers has the potential to improve the properties significantly at lower loading levels. Selection of low loading levels is important in order to tackle processing challenges and less defects into the composites.
7. It is imperative to consider using different silane coupling agents compatible with polyester and alumina nanofibers to evaluate their effects on mechanical properties at reduced viscosity and homogenous dispersion.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Tim Ferland of ANF Technology and Mr. David Gerald of Interplastic Corporation for their kind support in this research. The authors highly appreciate the help of Dr. Ray Cook, Jason Wagner, and Ruben Villarreal for waterjet cutting of test samples. The authors would also like to thank the Ms. Mariana Ocampo and Ms. Alissa Savage of ARSC

at Texas State University for the training and support for TEM and SEM Imaging. The authors are thankful to Arigbabowo Oluwasola and Elizabeth Alvizo of Advanced Composites Laboratory for their support and help at various stages of testing.

References

1. Crawford, R. and J. Throne, *ROTATIONAL MOLDING POLYMERS*. 2002. p. 19-68.
2. Chu, F., et al., *Hierarchical Structure: An effective Strategy to Enhance the Mechanical Performance and Fire Safety of Unsaturated Polyester Resin*. ACS Applied Materials & Interfaces, 2019. **11**(32): p. 29436-29447.
3. H. V. Boenig, *Unsaturated Polyesters, Structure and Properties*. Elsevier Publishing Company, Amsterdam 1964. 222 S., DIN A 5, Preis DM 31.—. Fette, Seifen, Anstrichmittel, 1966. **68**(1): p. 30-30.
4. Wang, S. and J. Qiu, *Enhancing thermal conductivity of glass fiber/polymer composites through carbon nanotubes incorporation*. Composites Part B: Engineering, 2010. **41**(7): p. 533-536.
5. Seyhan, A.T., et al., *Critical aspects related to processing of carbon nanotube/unsaturated thermoset polyester nanocomposites*. European Polymer Journal, 2007. **43**(2): p. 374-379.
6. Agnihotri, P., S. Basu, and K.K. Kar, *Effect of carbon nanotube length and density on the properties of carbon nanotube-coated carbon fiber/polyester composites*. Carbon, 2011. **49**(9): p. 3098-3106.
7. Jaya Vinse Ruban, Y., S. Ginil Mon, and D. Vetha Roy, *Mechanical and thermal studies of unsaturated polyester-toughened epoxy composites filled with amine-functionalized nanosilica*. Applied Nanoscience, 2013. **3**(1): p. 7-12.
8. Zhou, S.-X., et al., *Effect of nanosilica on the properties of polyester-based polyurethane*. Journal of Applied Polymer Science, 2003. **88**(1): p. 189-193.
9. Morote-Martínez, V., V. Pascual-Sánchez, and J.M. Martín-Martínez, *Improvement in mechanical and structural integrity of natural stone by applying unsaturated polyester resin-nanosilica hybrid thin coating*. European Polymer Journal, 2008. **44**(10): p. 3146-3155.
10. Marinkovic, A., et al., *Mechanical properties of composites based on unsaturated polyester resins obtained by chemical recycling of poly(ethylene terephthalate)*. Hemijska industrija, 2013. **67**: p. 913-922.
11. Mirabedini, S.M. and A. Kiamanesh, *The effect of micro and nano-sized particles on mechanical and adhesion properties of a clear polyester powder coating*. Progress in Organic Coatings, 2013. **76**(11): p. 1625-1632.
12. Albdiry, M.T. and B.F. Yousif, *Toughening of brittle polyester with functionalized halloysite nanocomposites*. Composites Part B: Engineering, 2019. **160**: p. 94-109.
13. Albdiry, M.T., H. Ku, and B.F. Yousif, *Impact fracture behaviour of silane-treated halloysite nanotubes-reinforced unsaturated polyester*. Engineering Failure Analysis, 2013. **35**: p. 718-725.
14. Saharudin, S.M., R. Atif, and F. Inam, *Effect of Short-Term Water Exposure on the Mechanical Properties of Halloysite Nanotube-Multi Layer Graphene Reinforced Polyester Nanocomposites*. Polymers, 2017. **9**(1).

15. Benny Cherian, A. and E.T. Thachil, *Toughening Studies of an Unsaturated Polyester Resin Using Maleated Elastomers*. Progress in Rubber and Plastics Technology, 2001. **17**(4): p. 205-224.
16. Yu, Z. and L.T. Drzal, *Functionalized graphene oxide as coupling agent for graphene nanoplatelet/epoxy composites*. Polymer Composites, 2019. **n/a**(n/a).
17. Lavoratti, A., A.J. Zattera, and S.C. Amico, *Mechanical and dynamic-mechanical properties of silane-treated graphite nanoplatelet/epoxy composites*. Journal of Applied Polymer Science, 2018. **135**(45): p. 46724.
18. Tee, D.I., et al., *Effect of silane-based coupling agent on the properties of silver nanoparticles filled epoxy composites*. Composites Science and Technology, 2007. **67**(11): p. 2584-2591.
19. Wan, Y.-J., et al., *Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide*. Composites Part A: Applied Science and Manufacturing, 2014. **64**: p. 79-89.
20. Ghosh, S., S.K. Goswami, and L.J. Mathias, *Surface modification of nano-silica with amides and imides for use in polyester nanocomposites*. Journal of Materials Chemistry A, 2013. **1**(19): p. 6073-6080.
21. Hao Wu, M.K.a.J.H.K. *Functionalized Nafen™ Alumina Nanofiber (ANF) Reinforced Polyamide 6 Nanocomposites: Mechanical, Thermal And Flame Retardant Properties*. in *Society for the Advancement of Material and Process Engineering*. 2015. Baltimore, MD.
22. I. Grodensky, A.R. *POLYMER NANOCOMPOSITES BASED ON NAFEN™ – UNIQUE ALUMINA NANOFIBERS*. in *Society for the Advancement of Material and Process Engineering* 2014. Seattle, WA.