Development of advanced composite materials: Defining the fabrication process for hybridization of graphene and natural silk reinforced epoxy composites

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Abstract: In structural applications, Epoxy resin finds extensive application for its low cost, high strength to low weight ratio, higher amenability with superior dimensional stability in elevated temperatures, and chemical inertness. Furthermore, graphene has been extensively used as reinforcement materials to enhance strength and tensile/flexural stiffness. In contrast, natural silk within the other natural fibres showed higher impact strength and ductility, good biodegradability, and excellent biocompatibility for a reinforcement filler material. Several ongoing field research on graphene and natural silk as an individual reinforcement in the epoxy composites have shown significant positive results. This paper concentrates on the research gap of hybridization of graphene and natural silk fibres (SF) as a combined reinforcement material to develop lightweight and high-performance epoxy composite material for structural applications. This paper discusses the suitable material selection and fabrication process for hybrid GO/SF epoxy composite. Graphene Oxide (GO) choice for the reinforcement on epoxy resin by (0,0.5,1,1.5,2,3 and 5) % volume fractions via wet transfer ultrasonication process and plain-woven Bombyx mori silk for 60% SF reinforcement discussed in the paper. The optimum volume fraction of GO and SF promoting significant improvements of the epoxy resin composites' mechanical properties needs further evaluation during material characterization.

Keywords: Graphene, Natural Silk, Epoxy composites, Advanced Composite Materials

1. Introduction:
Epoxy resins find extensive application for the production of lightweight structural composite materials due to their characteristic properties – High amenability with dimensional stability, good adhesion, chemical resistance, higher temperature extreme tolerance, high strength to weight ratio, low moisture absorption, along with fair mechanical properties at low cost [1-2]. Nevertheless, when get cured, the epoxies become brittle from the high degree of cross-linking leading to lower impact strength. Therefore, there is a necessity to modify monomers in the epoxy to upgrade the anticipated mechanical properties like a low creep, high modulus, strength, and outstanding thermal and chemical stability for structural application usage [3-4]. Epoxy resin is compatible with all standard reinforcements to enhance its impact strength and toughness [5-8].

Graphene is a single layer of carbon atoms into 2D honeycomb lattice packing with sp2 bonds. Graphene is very light (0.77 mg per m2), very flexible, and still has an excellent tensile strength of 130 GPa. This makes it an excellent reinforcement material for polymer composites. The graphene has a flat structure with an intuitive higher surface area (2630 square meters per gram). This characteristic property enables graphene to get dispersed into the matrix without any surface
modifications and makes it a good reinforcement material for the composites [9]. The mechanical and chemical properties of the matrix material become superior upon the addition of graphene due to the enhancement in strength and bonding between the graphene and matrix material [10]. Graphene fillers in the epoxy resin matrix increase the impact strength and toughness [11]. Further, graphene enhances the fire retardant for the epoxy resin matrix, which is essential for various industrial applications [12].

Silk is a natural protein fibre and is one of the strongest natural fibres. Silk has a lower density (1.3 x 103 Kgm-3), higher tensile strength (650-750 MPa), higher breaking energy (60 to 80 MJm-3), good elasticity, and excellent resilience. Natural silks are applied as a reinforcement filler medium, either as a single medium or combined with other filler materials in epoxy resin composites, to advance the mechanical properties, especially flexural and impact strength [13]. Inherently, silk fibres show excellent mechanical toughness as they can absorb and dissipate energy in parallel during deformation [14]. Silk as reinforcement filler improves the tensile and bending strength of epoxy composites [15]. Further, the usage of natural fibres in composites provides an option for biodegradable and bio-derived products.

Several ongoing field research on graphene and natural silk as an individual reinforcement in the epoxy composites have shown significant positive results. The present study focuses on the research gap of hybridization of graphene and natural silk fibres (SF) as a combined reinforcement material to develop lightweight and high-performance epoxy composite material for structural applications. The present study explores the novel concept for successfully integrating resilient and tough natural silk and strong and stiff graphene as reinforcement filler for epoxy resin composites for custom-built mechanical properties [16-17]. Moreover, based on the detailed review, it is expected that integration of tough natural silk and strong graphene could harmonize to fabricate advanced composite materials with enhanced properties fit for a broader scope of structural applications [16-17]. This paper defines the suitable material selection and fabrication process for hybrid GO/SF epoxy composite. However, the agglomeration effect and the optimum volume fraction of GO and SF promoting significant improvements of the epoxy resin composites' mechanical properties need to be studied during material characterization to understand the reinforcement's interfacial interaction with the epoxy resin matrix.

2. Material selection for the hybridization of graphene and natural silk reinforced epoxy composite

2.1 Graphene

Graphene and its derivatives have been applied openly in high-performance material research for property enhancements. In graphene, the stability of the sp2 bonds forming the hexagonal lattice counters the range of in-plane deformations, accounting for outstanding mechanical properties [18]. However, pure graphene is inherently unstable owing to the presence of the delocalized π electrons and agglomerates, apparently due to van der Waals interactions and high specific surface area [18]. Graphene oxide (GO) is stable with oxygen functional groups on the basal plane that take away the π-π stacking interactions and aggregation noted with pure graphene. GO is an extremely flexible material with the attributes of pure graphene and relatively simpler to process. GO is preferred over graphene nanoplatelets regularly due to the functional groups permitting filler and matrix bonding interactions, although the modulus of GO is only about 25% of that of monolayer graphene[18]. The reinforcement efficiency of GO does not get impacted by the number of GO layers [19]. GO has a similar structure to graphene with active hydroxyl, carboxyl, and epoxy groups on the surface and edge, allowing for strong hydrophilicity and provide an active structural basis for surface modification [20]. These characteristics give GO satisfactory composite capability and improve the dispersion of GO in the matrix resin. Moreover, GO is preferred for integrating with silk fibres due to its good uniform distribution solution.
characteristics [21]. The study shows that Graphene with a higher surface area and under 2% of volume fraction would provide higher results for augmentation of the mechanical properties [22]. During the hybridization, homogenous graphene dispersion in the matrix material needs to be ensured to avoid the formation of aggregates and failure points. The high surface area of reinforcement fillers enables load distribution over a large surface resulting in better performance.[16-17]. Hence GO reinforcement on epoxy resin by (0, 0.5, 1, 1.5, 2, 3, and 5) % volume fractions shall be considered for the study.

2.2 Natural Silk
Bombyx mori (BM) silk materials are often integrated with Graphene, GO, and Carbon Nanotubes to construct mechanically enhanced materials. BM silk fibre (SF) is a prominent natural fibre that exhibits excellent mechanical properties comparable to those of other plant fibres [23]. BM silk fibre has prominent features such as high ductility and strength due to its high crystallinity in molecular structure. The adding of silk fibre volume fractions in the epoxy composite enhanced the impact properties [24]. The silk fibre volume fraction of 30% by weight provided peak enhancements in young modulus, tensile strength, and elongation at break than the neat epoxy. The interfacial adhesions were improved, primarily resulting in improvement of the impact strength [25]. SF reinforced epoxy composites display considerable higher tensile strength and flexural strains at break than plant fibre and glass fibre reinforced composites [26]. Several noncovalent interactions in the SF/GO system enhance the composites' strength and toughness than their reinforcements [27]. Silk is also a suitable reinforcement medium as it permits a higher volume fraction (30 to 70%). A higher volume fraction of silk fibres expand the impact and flexural strength, tensile strength, and toughness of the matrix material. SF reinforcement to the extent of 70 vol% has been achieved in epoxy composites using compression moulding, and six times higher impact strength than neat epoxy @ 60 vol% of SF reinforcement was achieved [23]. A balanced weave pattern and the silk surface treatment are critical for stronger SF/epoxy interfacial adhesion and the advancement of mechanical properties. The moisture in silk fabric needs to be controlled before laminate fabrication. In another study, woven silk preform was a better choice than random silk preforms due to higher thickness variations and lower compaction, leading to lower fibre content [28]. Pressurized vacuum-assisted resin transfer moulding (VARTM) @ 30 psi allowed for uniform impregnation over silk preform resulting in the lesser void formation and strong adhesion. The specific flexural strength and modulus were increased by 30% and 65% over plain epoxy [24]. Hence, for the study, a plain-woven BM silk fabric around 90 GSM shall be used.

3. Fabrication of GO/SF epoxy composite
The GO/SF epoxy composite fabrication process has been briefed below [29-39] from the above literature study. The fabrication process for the hybrid composite is schematically shown in Figure 1.

1. The diglycidyl ether of Bisphenol-A (DGEBA) based epoxy resin with low viscosity shall be used for the matrix medium. The low viscosity enables easy flow of resin mixture in the VARTM. The curing ratio and the curing conditions shall be as per the resin manufacture recommendations.
2. A plain-woven BM silk fabric around 90 GSM shall be used for SF reinforcement.
3. The volume concentration of GO considered for the study is 0 %, 0.5%, 1% 1.5 %, 2%, 3%, and 5% by weight in the epoxy matrix.
4. GO volume fraction shall be introduced into epoxy resin via wet transfer by dispersing GO in ethanol through ultrasonication process for 2 hours before mixing with epoxy resin. The resultant mixture shall be placed in the oven at 60° C to remove excess ethanol, and stirring shall be continued for 24 hours to get a homogeneous mixture by maintaining at 50° C.
5. Hybrid GO/SF epoxy composite laminate comprising Silk fibre layers with a volume concentration of 60% shall be fabricated for various GO/epoxy volume concentrations using a VARTM set- up @ 30 psi to obtain a higher SF volume fraction with improved interfacial adhesion.
4. Conclusion
The study's work reveals a definite scope for positive hybridization effect, resulting in enhanced mechanical properties like modulus, ultimate stress, and toughness of Graphene/Silk epoxy composite compared with their reinforcement with epoxy composites. However, the characterization and agglomeration effect after combined reinforcement of Graphene and Silk to be studied in detail post the fabrications of the test samples to understand the interfacial interaction between the reinforcement fillers and epoxy resin matrix.

In this paper, the following conclusions on the material selection and fabrication process are arrived at for the hybridization of the Graphene/Silk epoxy composite, based on the research studies:

1. GO and BM silk selected for reinforcement with the low viscosity DGEBA epoxy resin. The concentration of GO shall be 0%, 0.5%, 1%, 1.5%, 2%, 3%, and 5% by weight in the epoxy matrix. A plain-woven BM silk fabric around 90 GSM was selected for the SF reinforcement.
2. GO will be introduced into epoxy resin via wet transfer and ultrasonication process.
3. Hybrid GO/SF epoxy composite laminate comprising SF layers with a volume concentration of 60% shall be fabricated for various GO/epoxy volume concentrations using a pressurized vacuum-assisted resin transfer moulding (VARTM) @ 30 psi and not through the wet-lay process, and
4. The schematic diagram (Figure 1) was established to process the hybrid GO/SF epoxy composite.

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References
[1] Harke 2006 Epoxy resin systems for composites Harke Chemical GmbH (Thailand) pp 1-20.
[2] A.B. Maureen, J M Cary and D N John  Epoxy Resin Hexcel Corporation.
[3] Njuguna J 2016 Lightweight composite structures in transport: design, manufacturing, analysis and performance (Woodhead Publishing)
[4] Pielichowski K and Njuguna J 2005 Thermal degradation of polymeric materials (Shawbury: Smithers Rapra Publishing)
[5] Mourad A-H I, Bekheet N, El-Butch, A A-Latif, Nafee D and Barton D C 2005 The effects of process parameters on the mechanical properties of die drawn polypropylene Polymer Testing 24(2) pp169-180
[6] Babaghayou M I, Mourad A-H I, Lorenzo V, Chabira S F and Sebaa M 2018 Anisotropy evolution of low-density polyethylene greenhouse covering films during their service life Polymer Testing 66 pp146-154.
[7] Babaghayou M I, Mourad A-H I, Ochoa A, Beltrán F and Cherupurakal N 2020 Study on the thermal stability of stabilized and unstabilized low-density polyethylene films Polymer Bulletin pp 1-17
[8] Babaghayou M I, Mourad A-H I, Lorenzo V, de la Orden M U, Urreaga J M, Chabira S F and Sebaa M, 2016 Photodegradation characterization and heterogeneity evaluation of the exposed and unexposed faces of stabilized and unstabilized LDPE films, Materials & Design, 111 pp279-290.
[9] Yuchi F, Lianjun W and Jianlin 2010 Preparation and electrical properties of graphene nanosheet/Al2O3 composites Carbon Science 48(10) pp 1743-49.
[10] Kuilla T, Bhadra S, Yao D, Kim N H, Bose S and Lee J H 2010 Recent advances in graphene-based polymer composites Progress in Polymer Science vol35 (11) pp1350–75.
[11] Reis J.M.L 2012 Effect of temperature on the mechanical properties of polymer mortars Materials Research 15(4)
[12] Liu S, Yan H, Fang Z, et al. 2014 Effect of graphene nanosheets on morphology, thermal stability, and flame retardancy of epoxy resin. Compos Sci Technol 90 pp 40–47.
[13] Shah DU, Porter D, Vollrath F 2014 Opportunities for silk textiles in reinforced bio composites: studying through-thickness compaction behaviour. Compos A Appl Sci Manuf 62:pp 1–10.
[14] Guan J, Porter D, and Vollrath F 2012 Silks cope with stress by tuning their mechanical properties under load Polymer 53(13) pp 2717–26.
[15] Shah DU, Porter D and Vollrath F 2014 Can silk become an effective reinforcing fibre? A property comparison with flax and glass reinforced composites. Compos.Sci.Technol. 101 pp 173–183
[16] Sanjeev K K, Sanjeev S, Mourad A-H I, PB Sharma (press, 2021) A literature review for development of advanced composites materials by reinforcement of epoxy composites with graphene and natural silk, Lecture notes in Mechanical Engineering.
[17] Sanjeev K K, Sanjeev S, Mourad A-H. I., PB Sharma 2020 Advanced composite materials: methodology for hybridization of graphene and natural silk reinforced epoxy composites Proceedings of the national conference on advancements & modern innovations in engineering and technology (Gurgaon- AMIET 2020) pp 62-65
[18] Dimitrios G P, I A Kinloch, and R J Young 2017 Mechanical properties of graphene and graphene-based nanocomposites Progress in Materials Science 90 pp 75–127
[19] Z Li, I A Kinloch, and R J Young 2016 The role of interlayer adhesion in graphene oxide upon its reinforcement of nanocomposites Philos Trans R Soc A 374
[20] Y H Fan, S W Yu, H M Wang, Y H Yao, Y Wang and C H Wang 2019 Study on preparation and properties of graphene reinforced epoxy resin composites IOP Conf. Series: Materials Science and Engineering 634 012044
[21] Y Wang, R Ma, K Hu, S Kim, G Fang, Z Shao and V V Tsukruk 2016 Dramatic enhancement of graphene oxide/silk nanocomposite membranes: increasing toughness, strength, and young's modulus via annealing of interfacial structures ACS Appl Mater Interfaces 8(37):24962-73
[22] Annamahesh A, Sunitha K, and Rangarajan S 2019 Study on mechanical behavior of graphene
based polymer composites II JITEE V8 I4.

[23] Yang K, Robert O R, Yizhuo G, Su J W and Juan G 2016 High volume-fraction silk fabric reinforcements can improve the key mechanical properties of epoxy resin composites Materials & Design 108 pp 470-478.

[24] Yang K, Su Jun W, Juan G, Zhengzhong S and Robert O R 2017 Enhancing the mechanical toughness of epoxy-resin composites using natural silk reinforcements Scientific reports 7, no. 1 pp 1-9.

[25] Zuraidah Z, Noor I S, Mohd Y and Mat U W 2020, Characteristics of continuous unidirectional silk fibre reinforced epoxy composites, Journal of Advanced Research in Materials Science 69, Issue 1 pp 16-28

[26] Shah DU, Porter D and Vollrath F 2014 Can silk become an effective reinforcing fibre? A property comparison with flax and glass reinforced composites. Compos. Sci. Technol. 101, pp 173–183

[27] Ren J, Liu Y, Kaplan D L. et al. 2019 Interplay of structure and mechanics in silk/carbon nanocomposites MRS Bulletin 44, pp 53–58

[28] Youssef K H, M. A Yalcinkaya, Gorkem E G ,Maya P M and Amirkhosravi, M C A 2018 34th International Conference of the Polymer Processing Society, (Taipei, Taiwan)

[29] Mourad A-H I, Cherupurakal N, Hafeez F B, I A Genena F, S Al Mansoori M and A Al Marzooqi L 2020. Impact Strengthening of Laminated Kevlar/Epoxy Composites by Nanoparticle Reinforcement Polymers 12(12) pp.2814.

[30] Mourad A-H I, Zaaroura N. and Cherupurakal N 2019 Wet lay-up technique for manufacturing of advanced laminated composites Karbala International Journal of Modern Science 5(1) p.5

[31] Mourad A-H I, Al Mansoori M S, Al Marzooqi LA, Genena F A and Cherupurakal N 2018 Optimization of curing conditions and nanofiller incorporation for production of high performance laminated kevlar/epoxy nanocomposites ASME Pressure Vessels and Piping Conference American Society of Mechanical Engineers Digital Collection.

[32] Fouad H, Mourad A-H I, ALshammari B A, Hassan M K, Abdallah M Y and Hashem M 2020 Fracture toughness, vibration modal analysis and viscoelastic behavior of kevlar, glass, and carbon fibre/epoxy composites for dental-post applications Journal of the mechanical behavior of biomedical materials 101 p.103456.

[33] Mourad A-H I, Idrisi A H, Zaaroura N, Sherif M M and Fouad H 2020 Damage assessment of nanofiller-reinforced woven kevlar KM2plus/epoxy resin laminated composites Polymer Testing, 86, p.106501.

[34] Mourad A-H I, Ayad O G, Rahman A, Hilal-Alnaqbi A and Abu-Jdayil B I 2016 Experimental investigation of kevlar KM2Plus nano-reinforced laminated composite thermo-mechanical properties ASME 2016 pressure vessels and piping conference American Society of Mechanical Engineers Digital Collection.

[35] Pathak A K, Borah M, Gupta A, Yokozeki T and Dhakate S R 2016 Improved mechanical properties of carbon fibre/graphene oxide-epoxy hybrid composites Compos Sci Technol 135 pp. 28-38.

[36] Change W, Kang Y, Yizhuo G, Jun X, Robert O.R and Juan G 2019 Mechanical properties and impact performance of silk-epoxy resin composites modulated by flax fibres, Composites Part A Applied science and manuf., V117,pp 357-368.

[37] Jamal I, Mourad A-H I, Fan Y, and Wood J T 2016 Through-thickness fracture behavior of unidirectional glass fibres/epoxy composites under various in-plane loading using the CTS test Engineering Fracture Mechanics 156 pp83-95.

[38] Ahmed W K, Mourad A-H I 2012. Using fibre reinforced polymer to restore deteriorated structural members. Int. J. Mat. Mech. Eng 11 1-7.

[39] Idrisi A H, Mourad A-H I, Abdel-Magid B, Mozumder M, and Afifi Y 2019 Impact of the harsh environment on E-glass epoxy composite ASME Pressure Vessels & Piping Conference American Society of Mechanical Engineers Digital Collection.