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EFFECT OF ZIRCONIA AND GRAPHENE NANOPARTICLES LOADING ON THERMO-MECHANICAL PERFORMANCE OF HYBRID POLYMER NANOCOMPOSITE

This study demonstrates the development of a unique hybrid thermoplastic composite using reduced Graphene oxide (rGO) content and Zirconia (ZrO_2) nanoparticles into the Ultra-High Molecular Weight Polyethylene (UHMWPE) biomaterials for continuous loading conditions. Specimens with different loadings of rGO (0 to 1.5 wt.%) and ZrO_2 (5 to 10 wt.%) were fabricated using liquid phase ultrasonication followed by the hot press moulding method. The samples were analyzed using Thermogravimetric Analysis (TGA), Impact (Izod) testing, and Dynamic Mechanical Analysis (DMA). The developed material feasibility was assessed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses. The findings revealed that the 1 wt.% rGO/5 wt.% ZrO_2/UHMWPE sample improved the storage modulus by 66.15%, and the Impact absorbed energy by 11.33% compared to the pristine UHMWPE. The proposed nanocomposite could be endorsed for artificial joints, prostheses, and other Artificial Bio-Bearing (ABB) applications.

Keywords: Zirconia; Graphene; Nanocomposite; UHMWPE; Polymer

1. Introduction

Over the last two decades, the mechanical and tribological performance of artificial implants and bio-liners components has become a prominent research area for academia and manufacturing industries. The tailored design, durability, ease of fabrication, and cost issue of polymeric implants are comparatively better than metallic orthopedic components [1]. The body parts of each person differ in design, working environment, loading condition, injury effect, and size of the persons. The varying design and shapes in the orthopedic component are critical issues for biomedical manufacturing industries. Another critical issue is the component or artificial implant loading condition during working hours, sometimes at higher temperatures and pressure than the ambient loading conditions could cause abnormal performance. It can lead to the failure of the product and causes accidental injuries. In this series, Ultra-High Molecular Weight Polyethylene (UHMWPE) is widely used in biomedical parts due to enhanced durability, wear resistance, and biocompatibility. Studies have proven that it could be recommended for orthopedic applications for high-loading conditions, but sometimes it fails under continuous fatigue loading due to limited thermomechanical characteristics [2]. UHMWPE's presence in the periprosthetic environment has also been linked to the onset of osteolysis and subsequent implant loosening. UHMWPE-based composites' tribological and mechanical efficiency can be enhanced by various treatments, including surface modifications, irradiation, and reinforcement supplement [3]. UHMWPE implants, however, have a short lifespan because of wear issues (due to cartilage damage, overweight, birth abnormalities, fractures, or bone-crushing) [4]. Among the various innovative methods, reinforcement with nanofillers has emerged a great deal in modern times. Various nanofillers such as Gold nanoparticles (AuNPs), Hydroxyapatite (HAp), Zinc Oxide (ZnO), Silver nanoparticles (AgNPs), Bioactive glass nanoparticles (BGn), Yttrium oxide (Y_2O_3), carbon nanotubes (CNTs), Multiwall carbon nanotubes (MWCNTs), Graphene nanoplatelets (GNPs), Aluminum Oxide (Al_2O_3), Graphene Oxide (GO) [5] are the broadly used approaches by eminent scholars in this field and hunt for better fillers is still going on. It has been noted that most investigations are limited to adding a single nanofiller; very little data exists on adding two or more types of filler material supplements.

In this series, Sughanthy et al. investigated the effect of HAp in a Polyethylene terephthalate (PET) matrix by the Dynamic mechanical analysis (DMA) test. They concluded that PET-HA nano-bio composite scaffold offers tissue engineering potential,

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and HA inclusion significantly improved the mechanical performance. The PET-HA nano-biocomposite scaffold consisting of 98% PET and 2% HA was preferred because it had lower storage and loss modulus than required for skin applications [6]. Duraccio et al. studied UHMWPE's mechanical and biological characteristics of (80-20 wt.%) Alumina Toughened Zirconia (ATZ). Both improvement in hardness and elastic modulus and Yield stress with the addition of small wt.% of (2.5%) ATZ. The developed composites showed good viscoelastic properties as per the findings of the DMA test. Dayyoub et al. elaborated on the effect of Graphene Nanoplates (GNPs) and Polyaniline(PANI) on the Structure and Mechanical Properties of UHMWPE Films. Functionalized GNPs reinforced UHMWPE sheets by deposition PANI. The effect of this functionalization seems to reduce the aggregation of fillers in the polymer matrix. Incorporating only 2 wt.% GNP/PANI shows improvement in crystallinity and tensile strength (45%). 1 wt.% GNP/PANI showed a 32% increase in young's modulus. The highest storage modulus was achieved by 2 wt.% UHMWPE/GNP/PANI. Also, compared to virgin UHMWPE films, the loss modulus values for the UHMWPE/GNP/PANI films had increased with higher film shape memory [7]. Maher et al. experimented on the ceramic(alumina) filler's impact properties for the effect of the acetabular liner. The liners are tested for 23, 21, 15, and 12 kN forces, and the tested samples stand in good condition with 12 kN suggesting impact is not always a factor behind ceramic liner failure[8]. The findings of Amurin et al. also highlight the improvement of impact properties of UHMWPE with little rGO (0.25 wt.%) content within the UHMWPE matrix, and the results decline at further incorporation of rGO. The rGO reinforcement provides a favorable effect on hardness, tensile strength, and wears resistance [9]. The findings of eminent scholars signify the desired improvement in the polymer matrix's mechanical, thermal and tribological aspects. Recently, innovative polymer composites incorporating graphene fillers have gained much interest. Among these fillers, reduced graphene oxide (rGO) has been accepted extensively due to its unique chemical functionality, electrical characteristics, superior aqueous solution dispersity, etc. Also, rGO can increase the mechanical properties of multifunctional polymer composites [10]. Zirconium dioxide (ZrO_2) has many applications owing to its exceptional features, such as high hardness, high elastic modulus, and high melting temperature [11].

Few studies were conducted on Reduced graphene oxide (rGO) nanoparticles as reinforcement in UHMWPE polymers. Also, it has been remarked that using Zirconium oxide (ZrO_2) and Reduced graphene oxide (rGO) as bifiller nanofillers is very limited in existing works. The purpose of using such a combination is that rGO has greater biosafety and stability in vivo than GO. For tissue engineering, cell culture, and other medicinal applications, rGO is a biocompatible class of material [12]. Zirconium is a transition metal with excellent corrosion resistance and increased mechanical, catalytic, and thermal qualities [13]. Both fillers have good biocompatibility and characteristics as needed by various biomaterials used in the human body. The present work aims to investigate the use of bifiller (rGO/ZrO_2) for UHMWPE base properties modification. An attempt has been made to overcome the constraints of conventional UHMWPE polymeric composites by using two nanofiller materials for improved physiomechanical performance. The current work aims to develop the cost-effective and mechanically efficient materials required for implants, prostheses, joint replacement, orthopedic, and other biomedical applications.

2. Experimentation

2.1. Method and methodology

Bio-nanocomposite fabrication is illustrated in Fig. 1. First of all, both the nanofillers Zirconia; ZrO_2 (30-50 nm) and

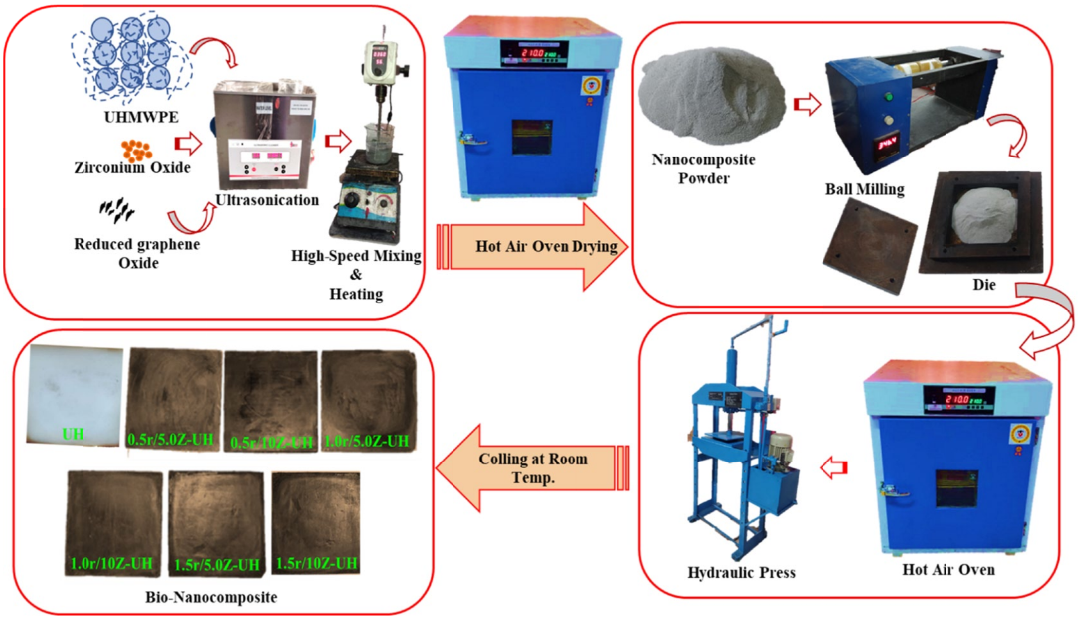

Fig. 1. Fabrication procedure of bifiller-modified nanocomposites

Reduced graphene oxide; rGO (98-99%, Green synthesized-Vitamin C) and UHMWPE Bio-medical grade (3×10^6 to 6×10^6 g/mol average molecular weight) are ultrasonicated for about 1 hour at 50 hertz (Hz) in three separated beakers in the presence of acetone (Purity % > 99%, Rankem) as a liquid medium for sonication. Afterward, all the mixtures are poured into a glass beaker and sonicated for another 60 minutes. The resultant mixture is stirred for 120 minutes at 450 revolutions per minute (rpm) at 75°C. This removes the maximum solvent traces from the mixture.

Followed by heating in a Hot air oven at 80°C until it gets dried. The resultant nonpowered mixture is then ball milled and filled in mild steel die, and silicone oil is used as a lubricant. The die is transferred to the hot air oven for 2 hours (@200°C) and hot-pressed (@100 bar) using a hydraulic machine.

After colling, the necessary American Society for Testing and Materials (ASTM) standards specimen is fabricated, as shown in TABLE 1. An in vitro study was conducted to study DMA, thermal stability, and Impact strength of ZrO_2/rGO modified UHMWPE nanocomposite samples.

2.2. Characterization of developed polymer nanocomposites

The dynamic mechanical investigation was carried out using a single simply supported beam model in a dynamic mechanical analyzer (DMA-NETZSCH-242 C, 80 mm (length) × 10 mm (width) × 4 mm (height)). DMA experiments were performed at temperatures ranging from ambient to 150°C, the test frequency is 1 Hz, nitrogen is introduced, and a heating rate of 3°C/min. Impact performance is tested (ASTM D256-63.5 mm × 12.7 mm × 3 mm) using an impact (Izod) testing equipment (TINIUS OLSEN 104) with an operating range of 0-25 J. At least three tests were carried out on each nanocomposite material of different compositions. The thermal stability is analyzed by TGA (Discovery-TGA 55, temperature accuracy ±1°C) for 30° to 700°C under a nitrogen environment. Also, FESEM (Tenscan) and EDAX (Ametek) are done to study the dispersion of bifiller in the polymer matrix.

3. Results and discussions

The thermal-mechanical characterization of neat UHMWPE and rGO/ZrO_2-based UHMWPE bio-nanocomposites was achieved via DMA tests TABLE 2 displays the physio-mechanical result of pure UHMWPE as well as a series of nanocomposites that include bi-fillers.

The DMA plots clearly exposed the increase in storage and loss moduli with increasing filler content in Mega Pascal (MPa). Fig. 2(a-c) shows the comparison of DMA results of pristine UHMWPE and various bifiller-filled bio nanocomposites. Fig. 2(a) shows that 0.5 wt.% rGO and 10 wt.%ZrO_2 filled UHMWPE does not significantly change in storage modulus compared to pristine UHMWPE. However, all other bio nanocomposites except 1 wt.% rGO and 10wt.%ZrO_2 showed improvement in storage modulus. Maximum enhancement is seen with 1 wt.%rGO and 5 wt.%ZrO_2 by 66.15% and 1.5 wt.%rGO and 10 wt.%ZrO_2 by 70.12% filled UHMWPE in comparison to pristine UHMWPE [14]. This increase in storage modulus gives excellent potential for reinforcement within the polymer matrix. The substantial increase in E′ was mainly attributed to the excellent dispersion of bifiller in the matrix and improved stress transfer between the matrix and bifiller [15]. As the temperature went up, the E' value showed a decline, which may be because of the side chain seg-

TABLE 1

Nomenclature of developed bio-nano composite

	Coding	Description	No. of samples
1	0.0r/0.0Z-UH	Pristine-UHMWPE	3
2	0.5r/5.0Z-UH	UHMWPE with 5.0% ZrO_2 and 0.5% rGO	3
3	0.5r/10Z-UH	UHMWPE with 10% ZrO_2 and 0.5% rGO	3
4	1.0r/5.0Z-UH	UHMWPE with 5.0% ZrO_2 and 1.0% rGO	3
5	1.0r/10Z-UH	UHMWPE with 10% ZrO_2 and 1.0% rGO	3
6	1.5r/5.0Z-UH	UHMWPE with 5.0% ZrO_2 and 1.5% rGO	3
7	1.5r/10Z-UH	UHMWPE with 10% ZrO_2 and 1.5% rGO	3

TABLE 2

Physio-mechanical result of pristine and bifiller UHMWPE nanocomposites

Sample Nomenclatures	E′ 30°C (MPa)	E″ 30°C (MPa)	T_g, tanδ (°C)	T_α (°C)
UH	911.54	107.21	119.27	56.51
0.5r/5.0Z-UH	1156.53	110.06	124.85	55.40
0.5r/10Z-UH	875.38	79.55	124.28	58.33
1.0r/5.0Z-UH	1514.60	124.27	126.68	59.98
1.0r/10Z-UH	694.05	56.98	122.17	60.59
1.5r/5.0Z-UH	1151.95	100.38	126.41	60.58
1.5r/10Z-UH	1550.76	135.28	127.18	61.02

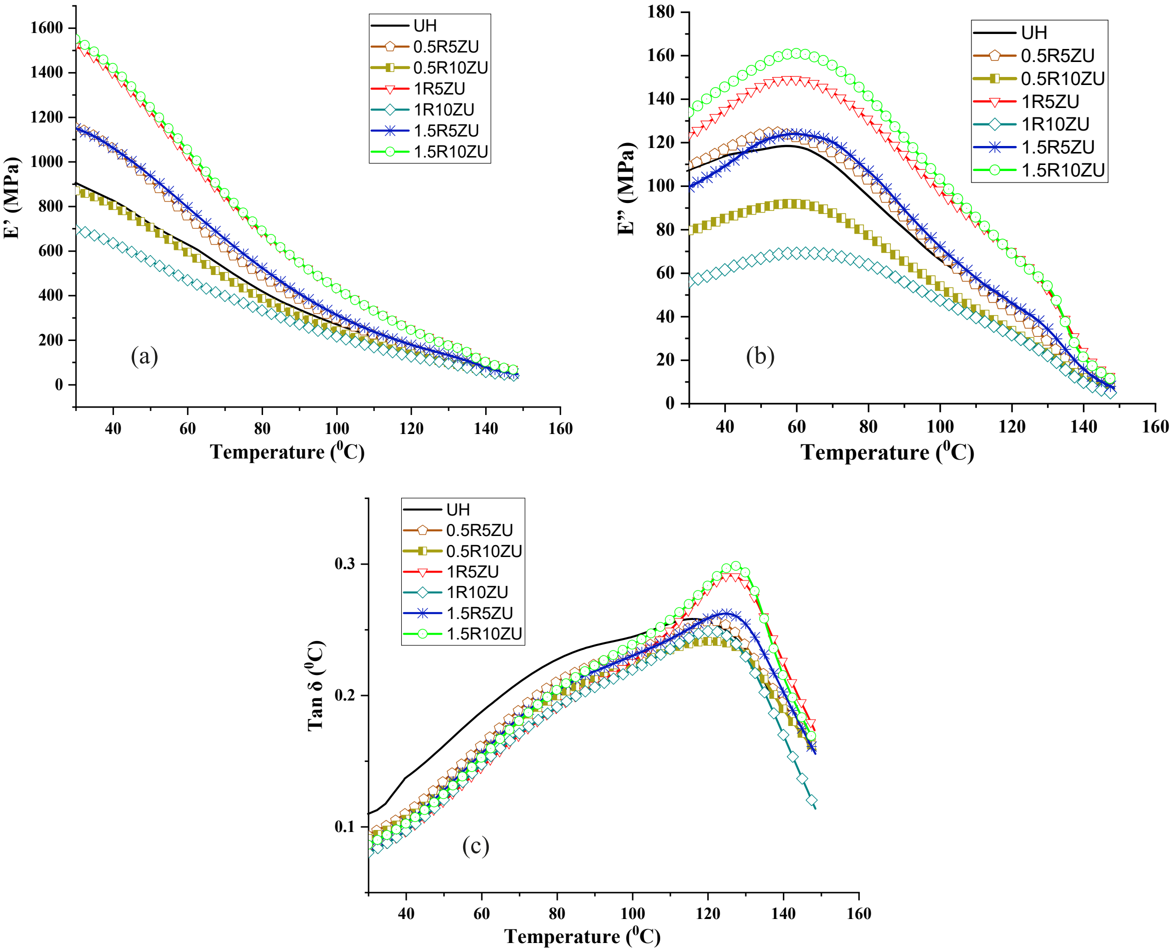

Fig. 2. (a) Describe the Storage modulus (E') MPa vs. Temperature (°C) plot for various developed bio-nanocomposites. (b) Describe the Loss modulus (E'') MPa vs. Temperature (°C) plot for various developed bio-nanocomposites. (c) Describe the Damping factor (tanδ) (°C) vs. Temperature (°C) plot for various developed bio-nanocomposites

ments' thermal motions because of the increased thermal energy. This is also because the physical interaction between the matrix and bifiller in the composites makes the mechanical interlocking stronger. However, when thermal motions increase, the polymer chain shrinks less across the nanoparticles, resulting in a smaller temperature-dependent rise in storage modulus. The decrease in storage modulus for 1 wt.% rGO and 10 wt.%ZrO_2 may be due to the combined effect of increased bifiller nanoparticles within the pristine polymer matrix, which may lead to aggregation and voids, thus reducing the extent of dispersion between bifiller and polymer matrix [16,17].

Energy dissipation in filled composites is commonly characterized by plotting the loss moduli (E'') vs. temperature plot (Fig. 2(b)). This relates to material stress and elongation. The loss modulus was observed to grow in relation to the amount of bifiller used. Moreover, adding bifiller causes the loss-peak width to expand, indicating that a more significant proportion of polymer chains contribute to the energy dissipation process due to the interaction between the matrix and the filler [17]. The E'' curve of UHMWPE exhibits a peak at 56.7°C. This can also be identified as an alpha star transition (Tα) associated with the slippage between crystallites, considering that it is a semicrystalline polymer [18]. Compared to pure UHMWPE, the loss modulus of the 1 wt.% rGO/5 wt.%ZrO_2/UHMWPE nanocomposite was higher. The prevailing viscous behavior of the rGO/ZrO_2/UHMWPE might account for these behaviors. The mechanical restraints of the materials may be increased by modification of the UHMWPE with rGO/ZrO_2, resulting in a lower degree of flexibility in the resulting rGO/ZrO_2 /UHMWPE nanocomposite [7,19]. Fig. 2(c) presents tan(δ) of pristine UHMWPE, and the rGO/ZrO_2 filled composites; slight improvement in glass transition temperature is shown in tan(δ) vs. temperature plots due to the addition of bifiller(rGO/ZrO_2). The Loss tangent as a function of temperature elaborates the damping response of rGO/ZrO_2/UHMWPE nanocomposite. A material's energy dissipation potential, or tan δ, is defined as the ratio of its viscous response to its elastic response. The damping parameter was found to be between 0.07 and 0.09 in the solid-state transition regime (β and γ transitions) [15]. The rGO/ZrO_2/UHMWPE composite with 1 wt.% rGO and 5 wt.%ZrO_2 had the lowest value of tanδ at a temperature of 30°C. The lowest value of tanδ at 30°C temperature for the rGO/ZrO_2/UHMWPE was obtained for 1 wt.% rGO and 5 wt.%ZrO_2. Thus, the composites exhibit a more elastic behavior [7]. It also showed that along with adding rGO/ZrO_2, the α peak shifted to a higher temperature; this specified that the melting temperature (T_m) of composite materials increased. Thus, of all the developed bio-nanocomposites 1 wt.% rGO and 5 wt.%ZrO_2 filled UHMWPE is the most suitable candidate in relation to Viscoelastic properties. Similar behavior was observed by Duraccio et al. studied the effect of alumina-zirconia loading in the UHMWPE polymer matrix [20]. This novel nanocomposite's improved mechanical processability might replace neat UHMWPE in biomedical applications such as acetabular cup liners, knee, shoulder, and finger joint wear components. It can also be used to develop external and internal prostheses.

The impact properties of any polymer matrix composite material are closely connected to the material's overall toughness. The Izod test gives information about the amount of kinetic energy needed to start a crack and let it spread to the point of failure. A rise in impact strength was observed in the bifiller-filled composites when rGO and ZrO_2 inclusions were added at various weight percentages, as shown in Fig. 3, compared to neat UHMWPE. This suggests that adding more rGO and ZrO_2-based nanofiller to the polymer matrix could help the composites absorb more impact energy. Because of the lubricating properties of rGO, the composite acquires a ductile character [21]. As a result, it can absorb a more significant impact while simultaneously protecting the core from direct impact. Because of this, higher impact energy would be required before the sample would crack [22]. The impact energy absorbed by neat rGO/ZrO_2-UH composite was found to be in the range of 2.601 to 2.896 J. However, in rGO/ ZrO_2-UH dispersed composite specimens, the highest impact energy was obtained in the 1.0% rGO and 5 wt.% ZrO_2 filled UHMWPE composite. Impact energy for UHMWPE-NEAT was 2.601 J, UHMWPE with 5.0% ZrO_2 and 0.5% rGO was 2.697 J, UHMWPE with 10% ZrO_2 and 0.5% rGO was 2.796 J, UHMWPE with 5.0% ZrO_2 and 1.0% rGO was 2.896J, UHMWPE with 10% ZrO_2 and 1.0% rGO was 2.489 J, UHMWPE with 5.0% ZrO_2 and 1.5% rGO was 2.840 J and UHMWPE with 10% ZrO_2 and 1.5% rGO was 2.675 J respectively.

The Impact energy for the 5.0% ZrO_2 and 1.0% rGO-UH was increased by 11.33% compared to the neat sample of UHMWPE. A similar trend was also observed in evaluating the impact strength of developed composite materials. Impact strength for 5.0% ZrO_2 and 1.0% rGO-UH is found to be 89.07 KJ/m^2, which is maximum in comparison to various developed samples obtained by the Izod test is the amount of kinetic energy required to originate a fracture and propagate the crack to the whole way through to the point of failure. Adding 5% ZrO_2 and 1% rGO into UHMWPE increases impact strength by forming cross-links or supramolecular bonds that shield the nanofillers and prevent crack propagation. Therefore, a bifiller (ceramic/carbon) addition to UHMWPE improves impact strength by preventing fracture propagation and wetting the nanofillers thoroughly. The impact strength was improved by using lower ceramic/carbon fillers content dispersed evenly throughout the UHMWPE matrix [23,24]. A negative trend is seen with higher filler loading. This may be due to the aggregation of nanofillers, resulting in the degradation of impact properties and the stress concentration within the polymer matrix. In the large particle agglomerations, cracks were able to propagate through weak places in the polymer matrix, resulting in the sample's brittleness and poor dispersion of particles in the composites; this causes a route of vulnerable regions inside the polymer matrix [24-26].

Scanning electron micrographs under high resolutions (5.00 kx) in Fig. 4 show that pristine and all other nanocomposites have lamellae and fibrillar junctions throughout the composites, as indicated in Fig. 4(a). Due to the excellent dispersion of bifiller (rGO and ZrO_2) within the polymer matrix (UHMWPE), robust interfacial interaction is observed, as shown in Fig. 4(b-d).

At 0.5 wt.% rGO and varying ZrO_2 wt.% (5 and 10 wt.%), a good interfacial connection is observed and is maximum in 1.0r/5.0Z-UH. With the incorporation of bifiller rGO and ZrO_2, the planer morphology of the composites becomes wavy (river-wave-like) and is increased with the increase of nanofiller amount within nanocomposites. The minor agglomeration zones are observable at lower filler content, as seen in 0.5r/10Z-UH, and are maximum at 1.0r//10Z-UH (Fig. 4(e-g)). Micro voids also rise with bifiller concentrations over 1 wt.% rGO and 5 wt.% ZrO_2. This decreases mechanical characteristics compared to the optimum sample (1 wt.% rGO and 5 wt.% ZrO_2) [27].

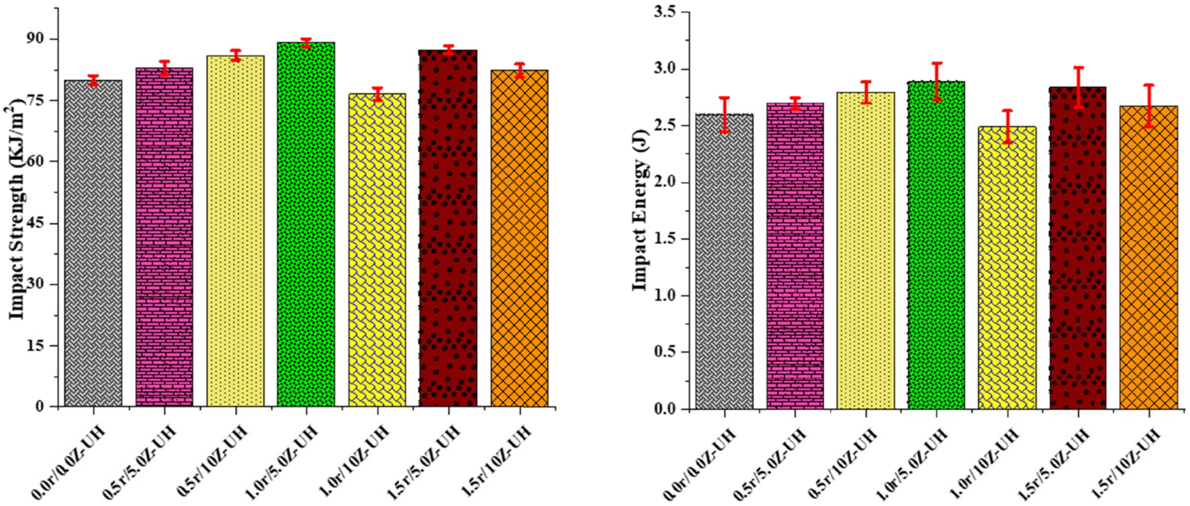

Fig. 3. Impact strength and impact energy graphs for various bio-nanocomposites

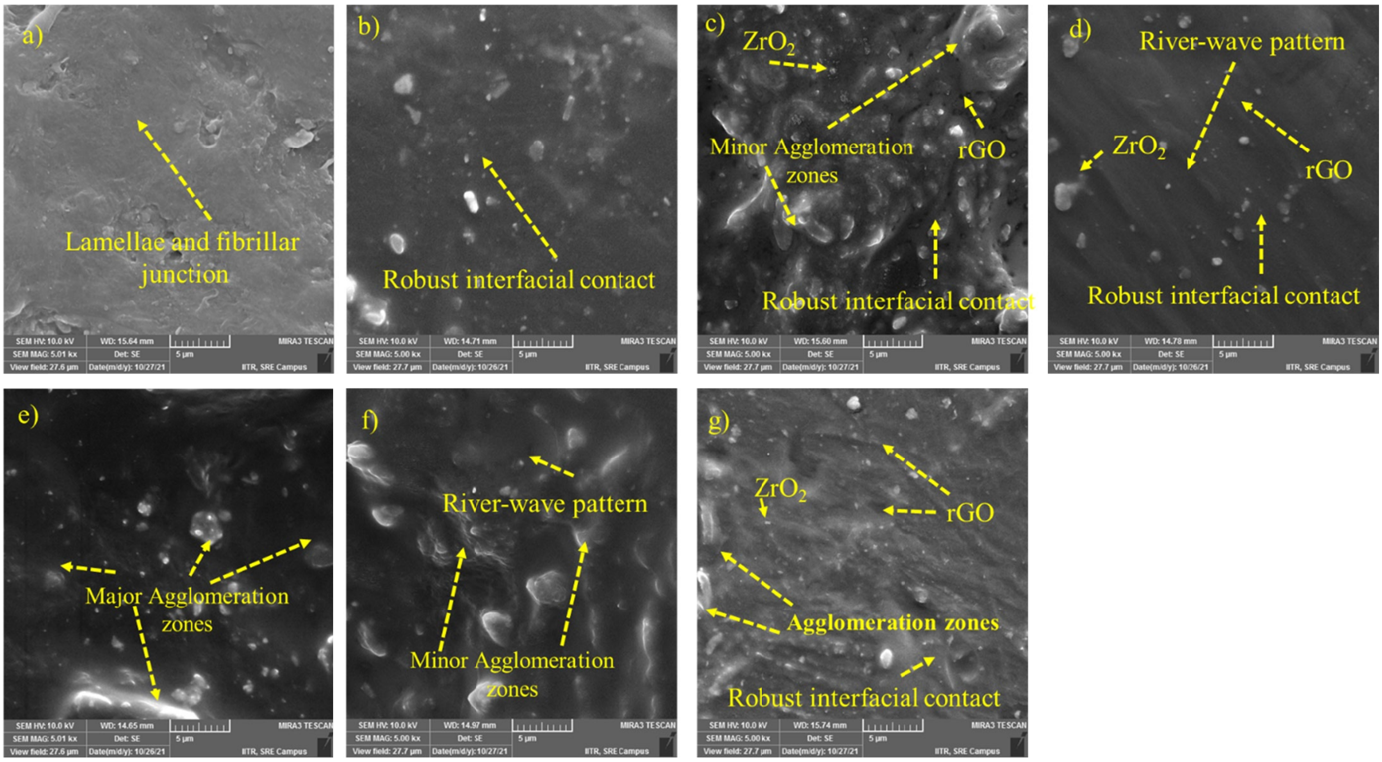

Fig. 4. SEM micrographs of: a) Pristine UHMWPE, b) 0.5r/5.0Z-UH, c) 0.5r/10Z-UH, d) 1.0r/5.0Z-UH, e) 1.0r/10Z-UH, f) 1.5r/5.0Z-UH, g) 1.5r/10Z-UH

As clearly seen from the EDAX results, the dispersion of bifiller within the polymer matrix is uniform throughout the matrix at lower wt.% of fillers content. The presence of oxygen throughout the nanocomposites shows the excellent distribution of rGO within the matrix. Fig. 5(a-b) shows EDAX scans of the pristine and 1.0r/5.0Z-UH. The Green, blue and red dots specify the amount of oxygen, zirconia, and carbon present within the nanocomposites due to the combined effect of matrix and rGO reinforcements.

EDAX suggests good dispersion, as indicated by SEM micrographs. Also, the sum spectra obtained by EDAX Scan highlight the peaks for various elements present in the developed nanocomposites [11]. From the combined results, it can be stated that the adopted methodology is relatively superior and suitable for the development of highly physio-mechanical properties enriched specimens.

TGA of pure UHMWPE and rGO/ZrO_2/UHMWPE blends was carried out to assess the effects of blend composition on the thermal stability of the polymers. Thermo-gravimetric (TG) curves of UHMWPE and its composites are shown in Fig. 6. Virgin UHMWPE decomposition curves had 5 areas characterized by 4 temperature points [28] T_0, T_1, T_2, and T_3. At first, the weight of the sample stays constant, but then it gradually increases until it reaches a peak at T_0. The melting of the crys-

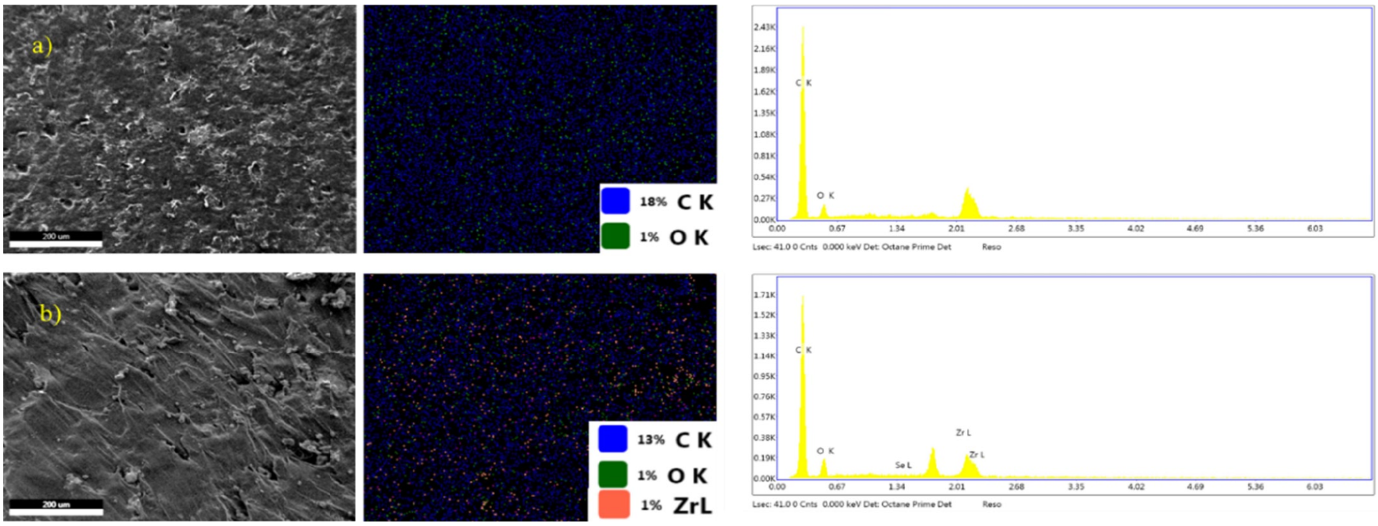

Fig. 5. EDAX results of: (a) Pristine UHMWPE (b) 1.0r/5.0Z-UH

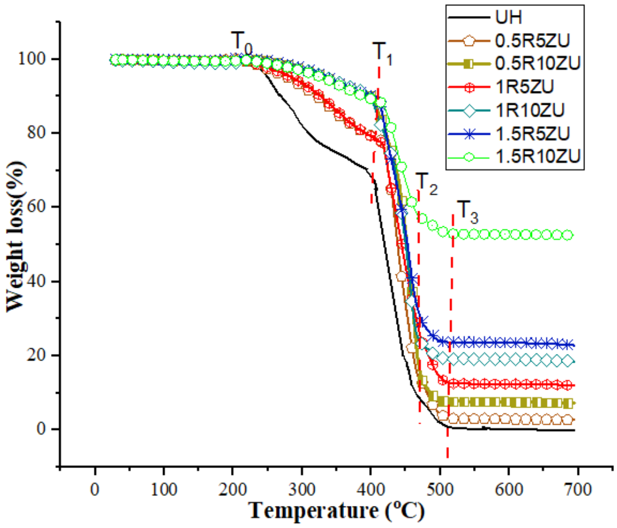

Fig. 6. TGA scan for various developed bio-nanocomposites

talline components of the UHMWPE releases some air into the sample. Once the oxidation cycle begins, samples lose mass at a non-linear rate until T_1. Afterward linear decline in sample weight is noticed due to pure thermal deterioration from T_1 to T_2. When heated to T_3, after complex oxidation and volatilization, the residue is left only. The TG curves of rGO/ZrO_2/UHMWPE composites are similar in form to those of the neat polymer but with minor differences in the slopes of the curves and the locations of the temperatures that compose the separate degradation zones (TABLE 3). When compared to the unfilled polymer, T_0 doesn't change much for any of the nanocomposites. With the increase in bifiller (rGO/ZrO_2) content within the UHMWPE for T_0-T_1 (range), with increasing the rGO/ZrO_2, the slope of the weight loss gets steeper.

On the other hand, T_1 is the same for both pure polymers, 1.0r/10Z-UH and 0.5r/10Z-UH, whereas all other nanocomposites show an increase of T_1 temperature. The T_2 and T_3 show improvement in all bifiller-filled nanocomposites. From the above study, it can be assessed that adding rGO and ZrO_2 favors the thermal stability of the developed nanocomposites. Also, the residue left after 700°C temperature for nanofiller (rGO/ZrO_2) filled polymer matrix suggests improved thermal stability of the developed nanocomposites. A similar trend is found by Duraccio et al. [20] and Yousef. et al. [29] with alumina-zirconia and graphene oxide.

TABLE 3

Decomposition temperatures of UHMWPE and rGO/ZrO_2/UHMWPE nanocomposites by TGA

Samples	T_o (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)
UH	223 ±1	403±1	467±1	510±1
0.5r/5.0Z-UH	204±1	417±1	468±1	510±1
0.5r/10Z-UH	223±1	403±1	474±1	512±1
1.0r/5.0Z-UH	212±1	416±1	476±1	514±1
1.0r/10Z-UH	223±1	403±1	469±1	514±1
1.5r/5.0Z-UH	216±1	411±1	470±1	515±1
1.5r/10Z-UH	221±1	417±1	469±1	519±1

4. Conclusion

In this paper, the rGO/ZrO_2 was used to improve the thermal, dynamic mechanical, and impact of the UHMWPE polymeric material used in various articulation liners of the human body. The conclusions of the investigation of morphological and various testing are discussed below:

1. The produced polymeric nanocomposite exhibits strong adhesion between fillers and matrix for 1 wt.% rGO and 5 wt.%ZrO_2, as determined by SEM and energy dispersive X-ray spectroscopy. The EDAX also demonstrates the efficacy of ultrasonication and ball milling in dispersing rGO and ZrO_2 fillers at 1 wt.% and 5 wt.%, respectively.
2. According to DMA and Izod impact findings, 1 wt.% rGO and 5 wt.% ZrO_2 nanoparticles in UHMWPE may serve as efficient reinforcement by increasing viscoelastic stiffness and Impact strength.
3. Storage modulus values for the rGO/ZrO_2/UHMWPE nanocomposite were increased for lower rGO, and ZrO_2 content compared to pristine UHMWPE and are highest for 1 wt.% rGO and 5 wt.% ZrO_2 content composite.
4. The loss modulus of the rGO/ZrO_2/UHMWPE nanocomposite of 1 wt.% rGO and 5 wt.%ZrO_2 was higher than the loss modulus of the virgin UHMWPE, which means that there had been a decrease in the flexibility of the developed nanocomposite with lower filler content. For 10 wt.% ZrO_2, both storage modulus and loss modulus decline compared to unfilled polymer indicating unstable structure and large accumulation zones.
5. TGA results suggest the improvement of thermal stability of all the developed nanocomposites with respect to pristine UHMWPE. These temperature ranges are highly desired for bio-bearing component development.

This study shows that ZrO_2/rGO nano-fillers can efficiently produce bio nanocomposite samples in different nanofiller percentages. This combination has increased the impact strength and thermomechanical performance. An improvement of 11.33% is observed for impact energy in 1 wt.% rGO and 5 wt.% ZrO_2 composite with respect to pristine UHMWPE. The bifiller-reinforced nanocomposite (ZrO_2/rGO-UHMWPE) can be endorsed for the production of prostheses, liner materials in joint replacement, and Artificial Bio-Bearing (ABB) components. Therefore, based on the above study's findings, 1 wt.% rGO and 5 wt.% ZrO_2 may be a decent choice for manufacturing acetabular cub liners and fabricating various joints and internal-external implants with superior mechanical capabilities compared to pristine UHMWPE. In the future, the inclusion of another type of carbon-based nanoparticles (CBNs) could be tested for other configurations of orthopedic components.

REFERENCES

[1] T.T. Dang, M. Nikkhah, A. Memic, A. Khademhosseini, Polymeric Biomaterials for Implantable Prostheses, in: S.G. Kumbar,

C.T. Laurencin, M. Deng (Eds.), Natural and Synthetic Biomedical Polymers 2014, Elsevier Inc. 2014.
DOI: https://doi.org/10.1016/B978-0-12-396983-5.00020-X

[2] R. Scholz, M. Knyazeva, D. Porchetta, N. Wegner, F. Senatov, A. Salimon, S. Kaloshkin, F. Walther, Development of biomimetic in vitro fatigue assessment for UHMWPE implant materials, J. Mech. Behav. Biomed. Mater. **85** (5), 94-101 (2018).
DOI: https://doi.org/10.1016/j.jmbbm.2018.05.034

[3] D.K. Singh, R.K. Verma, Contemporary Development on the Performance and Functionalization of Ultra High Molecular Weight Polyethylene (UHMWPE) for Biomedical Implants. Nano Life **11** (03), 2130009 (2021).
DOI: https://doi.org/10.1142/s1793984421300090

[4] K. Mordal, A. Szarek, Analysis of Stresses and Strains Distribution of Polyethylene Cups in Hip Joint Endoprosthesis at Various Articular Joints and Friction Conditions. Arch. Metall. Mater. **66** (2), 523-530 (2021).
DOI: https://doi.org/10.24425/amm.2021.135888

[5] S.G.A. Park, Abdal-Hay, J.K. Lim, Biodegradable poly (lactic acid)/multiwalled carbon nanotube nanocomposite fabrication using casting and hot press techniques. Arch. Mech. Eng. **60** (2), 1557-1559 (2015).
DOI: https://doi.org/10.1515/amm-2015-0172

[6] S.A.P. Sughanthy, M.N.M. Ansari, A. Atiqah, Dynamic mechanical analysis of polyethylene terephthalate / hydroxyapatite biocomposites for tissue engineering applications. J. Mater. Res. Technol. **9** (2), 2350-2356 (2020).
DOI: https://doi.org/10.1016/j.jmrt.2019.12.066

[7] T. Dayyoub, A.V Maksimkin, S. Kaloshkin, E. Kolesnikov, D. Chukov, T.P. Dyachkova, I. Gutnik, The structure and mechanical properties of the UHMWPE films modified by the mixture of graphene nanoplates with polyaniline. Polymers (Basel). **11** (1), 1-14 (2019).
DOI: https://doi.org/10.3390/polym11010023

[8] S.A. Maher, J.D. Lipman, L.J. Curley, M. Gilchrist, T.M. Wright, Mechanical performance of ceramic acetabular liners under impact conditions. J. Arthroplasty **18** (7), 936-941 (2003).
DOI: https://doi.org/10.1016/S0883-5403(03)00335-8

[9] L.G. Amurin, M.D. Felisberto, F.L.Q. Ferreira, P.H.V. Soraes, P.N. Oliveira, B.F. Santos, J.C.S. Valeriano, D.C. de Miranda, G.G. Silva, Multifunctionality in ultra-high molecular weight polyethylene nanocomposites with reduced graphene oxide: Hardness, impact and tribological properties. Polymer (Guildf). **240**, 124475 (2022).
DOI: https://doi.org/10.1016/j.polymer.2021.124475

[10] G. Pavoski, T. Maraschin, M.A. Milani, D.S. Azambuja, R. Quijada, C.S. Moura, N. de Sousa Basso, G.B. Galland, Polyethylene/reduced graphite oxide nanocomposites with improved morphology and conductivity. Polymer (Guildf). **81**, 79-86 (2015).
DOI: https://doi.org/10.1016/j.polymer.2015.11.019

[11] M. Salari, S. Mohseni Taromsari, R. Bagheri, M.A. Faghihi Sani, Improved wear, mechanical, and biological behavior of UHMWPE-HAp-zirconia hybrid nanocomposites with a prospective application in total hip joint replacement. J. Mater. Sci. **54** (5), 4259-4276 (2019).
DOI: https://doi.org/10.1007/s10853-018-3146-y

[12] S. Kesarwani, R.K. Verma, A Critical Review on Synthesis, Characterization and Multifunctional Applications of Reduced Graphene Oxide (rGO)/Composites. Nano **16** (9), 2130008 (2021).
DOI: https://doi.org/10.1142/S1793292021300085

[13] E.A. Albanés-Ojeda, R.M. Calderón-Olvera, M. García-Hipólito, D. Chavarría-Bolaños, R. Vega-Baudrit, M.A. Álvarez-Perez, O. Alvarez-Fregoso, Physical and chemical characterization of PLA nanofibers and PLA/ZRO2 mesoporous composites synthesized by air-jet spinning. Indian J. Fibre Text. Res. **45** (1), 57-64 (2020).

[14] E.H. Backes, L.D.N. Pires, C.A.G. Beatrice, L.C. Costa, F.R. Passador, L.A. Pessan, Fabrication of Biocompatible Composites of Poly (lactic acid)/Hydroxyapatite Envisioning Medical Applications. Polym. Eng. Sci. **60** (3), 636-644 (2020).
DOI: https://doi.org/10.1002/pen.25322

[15] H.S. Jaggi, S. Kumar, D. Das, B.K. Satapathy, A.R. Ray, Morphological correlations to mechanical performance of hydroxyapatite-filled HDPE/UHMWPE composites. J. Appl. Polym. Sci. **132** (1), 1-10 (2015). DOI: https://doi.org/10.1002/app.41251

[16] M.A. Bashir, Use of Dynamic Mechanical Analysis (DMA) for Characterizing Interfacial Interactions in Filled Polymers. Solids. **2** (1), 108-120 (2021).
DOI: https://doi.org/10.3390/solids2010006

[17] K. Sewda, S.N. Maiti, Dynamic mechanical properties of high-density polyethylene and teak wood flour composites. Polym. Bull. **70** (10), 2657-2674 (2013).
DOI: https://doi.org/10.1007/s00289-013-0941-0

[18] L.M. Lozano-Sánchez, I. Bagudanch, A.O. Sustaita, J. Iturbe-Ek, L.E. Elizalde, M.L. Garcia-Romeu, A. Elías-Zúñiga, Single-point incremental forming of two biocompatible polymers: An insight into their thermal and structural properties. Polymers (Basel). **10** (4), 391 (2018).
DOI: https://doi.org/10.3390/polym10040391

[19] Y.A. Kang, S.H. Oh, J.S. Park, Properties of UHMWPE fabric reinforced epoxy composite prepared by vacuum-assisted resin transfer molding. Fibers Polym. **16** (6), 1343-1348 (2015).
DOI: https://doi.org/10.1007/s12221-015-1343-8

[20] D. Duraccio, V. Strongone, G. Malucelli, F. Auriemma, C. De Rosa, F.D. Mussano, T. Genova, M.G. Faga, The role of alumina-zirconia loading on the mechanical and biological properties of UHMWPE for biomedical applications. Compos. Part B. **164** (1), 800-808 (2019).
DOI: https://doi.org/10.1016/j.compositesb.2019.01.097

[21] D. Berman, A. Erdemir, A.V. Sumant, Graphene: A new emerging lubricant. Mater. Today. **17** (1), 31-42 (2014).
DOI: https://doi.org/10.1016/j.mattod.2013.12.003

[22] N. Dalai, P.S.R. Sreekanth, UHMWPE / nanodiamond nanocomposites for orthopaedic applications: A novel sandwich configuration-based approach. J. Mech. Behav. Biomed. Mater. **116** (9), 104327 (2021).
DOI: https://doi.org/10.1016/j.jmbbm.2021.104327

[23] I.N. Safi, H.K. A., Ali N.A., Assessment of zirconium oxide nano-fillers incorporation and silanation on impact, tensile strength and color alteration of heat polymerized acrylic resin. J. baghdad Coll. Dent. **24** (2), 36-42 (2012).

[24] S. Watcharamaisakul, B. Sindhupakorn, A. Lepon, Effect of Graphite Addition on Mechanical Properties of Uhmwpe for Use as Tibia Insert Bio composite Materials. Suranaree J. Sci. Technol. **24** (2), 105-111 (2017).

[25] A. Kiziltas, S. Tamrakar, J. Rizzo, D. Mielewski, Characterization of graphene nanoplatelets reinforced sustainable thermoplastic elastomers. Compos. Part C Open Access. **6** (7), 100172 (2021). DOI: https://doi.org/10.1016/j.jcomc.2021.100172

[26] B. Suresha, A. Padaki, A. Jain, B. Kumar, A.A. Kulkarni, Role of Zirconia Filler on Mechanical Properties of HDPE/UHMWPE Blend Composites. Appl. Mech. Mater. **895**, 272-277 (2019). DOI: https://doi.org/10.4028/www.scientific.net/amm.895.272

[27] B.J. Ash, R.W. Siegel, L.S. Schadler, Mechanical Behavior of Alumina/Poly (methyl methacrylate) Nanocomposites. Macromolecules **37** (4), 1358-1369 (2004).
DOI: https://doi.org/10.1021/ma0354400

[28] S. Suñer, R. Joffe, J.L. Tipper, N. Emami, Ultra-high molecular weight polyethylene/graphene oxide nanocomposites: Thermal, mechanical and wettability characterization. Compos. Part B Eng. **78**, 185-191 (2015).
DOI: https://doi.org/10.1016/j.compositesb.2015.03.075

[29] N. Yousefi, X. Lin, Q. Zheng, X. Shen, J.R. Pothnis, J. Jia, E. Zussman, J.K. Kim, Simultaneous in situ reduction, self-alignment and covalent bonding in graphene oxide/epoxy composites. Carbon **59**, 406-417 (2013).
DOI: https://doi.org/10.1016/j.carbon.2013.03.034