Structure and properties of polystyrene/graphene oxide nanocomposites

Zaid G. Mohammadsalih^a and Noor S. Sadeq^b

^aApplied Science Research Unit, Applied Science Department, The University of Technology, Baghdad, Iraq; ^bMaterials Science Branch, Applied Science Department, The University of Technology, Baghdad, Iraq

ABSTRACT

The addition of graphene as an efficient nano-filler to different polymer matrices lead to a substantial improvement in different physical properties which, as a result, pave the way towards promising applications. In this work, Polystyrene (PS) was reinforced with different low loadings of graphene oxide (GO). The latter was prepared according to the Hummers method. The incorporated weight fractions were (0.01, 0.05, 0.1, 0.25, 1.0) wt. %. Solution blending was the adopted approach to prepare the nanocomposites. The resulted nanocomposites were characterised compared to the neat polymer. Many tools were employed to investigate the structure, morphology, thermal, and thermo-mechanical behaviour of GO, neat polymer, and the nanocomposites. The structural and morphological outcome for GO and PS was confirmed compared to the literature. The outcome confirmed as well the good dispersion of GO nano-sheets in the PS. The thermal and thermo-mechanical properties were enhanced for the nanocomposites compared to the neat polymer. The results emphasised the improvement of nanocomposites' performance as the inclusion of GO went higher. **ARTICLE HISTORY**

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1. Introduction

Carbon based nano-fillers for a range of applications have recently attracted a considerable attention due to their exceptional mechanical and physical properties such as high strength, high stiffness and high thermal and electrical conductivities. Many of research groups have prepared and study the features of these materials according to their low cost, low weight and ease of processing.^[1] Graphite, fullerene, carbon nano-tubes and the recently discovered material, graphene, are derived from this fascinating material, carbon, and they are the most widely studied allotropes of interest to technologists and researchers due to their unique applications in various fields.^[2]

Graphene is a planar honeycomb lattice that is a two dimensional, one atom thick carbon sheet. Its properties include high thermal conductivity, high intrinsic electron mobility, optical transmittance of 98%, large specific surface area and high Young's modulus.^[3] These properties offer graphene the potential for numerous different applications in many disciplines such as sensors, energy conversion, storage devices, solar cells and reinforced composites.^[4] To enable the exploitation of these unique properties in applications, graphene and its derivatives have been successfully prepared using different routes such as bottom-up chemical vapour deposition and top down exfoliation of graphite by means of oxidation, intercalation and/or sonication.^[5]

As a consequence of their high Π - Π interactions (kind of non-covalent interaction between electron rich Π system

and another molecule), graphene sheets are not directly mixed with the polymer matrices to produce polymer nanocomposites as the graphene sheets tend to stack into large aggregates. For this reason, graphene oxide is usually incorporated into polymer matrices for making high quality polymer nanocomposites, as it has better compatibility with polymers, forms a uniform dispersion and offers a possibility of mass production.^[6]

The structure of GO may be considered as a graphene sheet with attached oxygen functional groups in the forms of carboxyl and hydroxyl groups at the edges and epoxy groups and some carbonyl groups in the basal plane (Mkhoyan et al. 2009; Liao et al. 2011).^[7,8]

Polystyrene (PS) is one of the most common widely used thermoplastics. It can be used in many kinds of applications such as construction, automotive, protective packaging etc. The annual commercial consumption for this material has exceeded the barrier of billion kilogram.^[9] The combination of nano-fillers that have at least one dimension in the nanoscale (1-100) nm and the polymer matrix are known as nanocomposites.^[10] Nanocomposites have been synthesised by university researchers and private sector organisations with a view to developing applications in a number of markets such as aerospace, sports products, automobiles etc..^[11] A substantial improvement in polymer nanocomposites' performance can be achieved at very low loadings of nanofillers. The GO based graphene materials are showing a remarkable improvement in different properties at very low loadings as these nano-fillers possess high aspect ratio and

large interfacial area that makes the low loadings of these nano-fillers sufficient to achieve the required improvement.^[12] This will be important for manufacturing materials that have lighter weight but that are also stronger.^[13]

A research group^[14] was confirmed that adding only 1.0 wt. % of GO to polyethylene oxide PEO led to a 260% improvement in thermo-mechanical stability for the polymer that was used in lithium-ion battery applications. This result was achieved according to the superior properties of GO and the strong interfacial interaction between GO and the surrounding PEO.

2. Experimental section

2.1. Materials, preparation of graphite oxide, GO, and nanocomposites

Materials employed in this work were reported previously in a recent literature.^[15] Improved Hummers method was adopted to prepare graphite oxide as reported by collaborators in their co-work.^[16] 6 g of graphite was mixed with 3 g of NaNO₃ in a beaker. 138 ml of high concentrated H₂SO₄ (98%) was added to the beaker which was put in an ice bath to keep the reaction temperature below 35 °C. Then, 36 g of KMnO₄ was added cautiously over 2 days. A magnetic stirrer was employed to mix the aforementioned chemicals at a speed of 200 rpm.

This resulted in a yellow brown viscous mixture. To which 10-15 ml of H₂O₂ was added in order to quench the reaction. 400 ml of distilled water and 100 ml of HCL was then used for reducing the acidity of the graphite oxide. A centrifugation process was performed as centrifuges of (Richmond scientific limited, UK and Eppendorf, Germany) were utilised for many times after adjustment to 8000 rpm for 1 hour each time and the graphite oxide was washed with distilled water over 18h till the pH of the solution reached 5.5. The GO was then prepared by freeze drying technique according to a specific procedure adopted by some researchers.^[17] The graphite oxide was sonicated for 1h (Fisher brand Elma, Germany) and centrifuged for 30 minutes at 6000 rpm. The suspension was then casted into Teflon coated metal tray and left to be frozen in a freezer for 24 h at -40 °C. The GO then was then kept inside the chamber of a freeze drying machine (Bradley refrigeration. Edwards, UK) for 48 h under a pressure around 10^{-1} bar. The final product of GO by this procedure was a fluffy powder (porous foam) material. The nanocomposites samples were prepared by solution blending using THF. An optimum approach of preparation concluded by co-authors^[15] was adopted to prepare samples.

20 g of PS pellets were dissolved in 200 ml of THF using magnetic stirring for 2 h at 600 rpm. Different amounts of GO were suspended in specific volumes of THF for each concentration. The weight fractions for GO in PS/GO nano-composites were (0.01, 0.05, 0.1, 0.25 and 1.0) wt. % beside the neat polymer.

The suspensions of GO/THF were stirred for 2 h at 600 rpm and pre-sonicated for 30 min. Each concentration of GO/THF suspension was mixed with 200 ml of PS/THF

solution. The mixed solutions were stirred for 1:30 h. Then, to ensure a good dispersion of GO nanosheets in PS matrix, a bath sonication (Fisherbrand, Germany) was used for 0.5 h and shear mixing (Silverson, UK) was used for 1 h at mixing speed of 1600 rpm/Amp 0.3. The obtained suspension of PS/GO was poured in a glass covered Petri-dishes to ensure a slower evaporation for the solvent. All samples were left in a fume cupboard for 1 week and then in a vacuum oven for 3 hours at 40 $^{\circ}$ C to be fully dried.

2.2. Characterisation

For AFM, 2 ml of graphite oxide was mixed and stirred with 200 ml of distilled water. This mixture has sonicated and centrifuged for 30 minutes each. An aqueous suspension of GO was formed via sonication in bath sonicator which led to direct exfoliation. This approach was adopted by some researchers.^[18] Small drops were taken from the solution and precipitated over small black sheet that had been taped over a slide of glass and this was followed by mechanical exfoliation using scotch tape. The slide was left overnight to dry for AFM imaging purposes. The AFM measurements were carried out on a (3100 dimension, CLI digital instrument, USA) for finding the lateral size and thickness of graphene sheet. Real time scanning was carried out at ambient temperature and the image was recorded using Nanoscope software.

Non-contact-tapping mode was used to characterise the graphene. The tip used for imaging was made from silicon by Nanosensors ^{TM,} (Switzerland) and it had a 'diving board' shape with resonant frequency of 210-490 KHz.

An optical microscope (Swift, New York Microscope Co. USA) was used for imaging the nanocomposite samples to determine the distribution of GO in the PS matrix. The microscope had a resolution of 10X with a magnification scale of 0.5 mm.

For investigation the quality of dispersion of the nanosheets in the matrix, and to obtain an idea about the morphology of the pristine polymer, transmission electron microscopy (TEM) was used. Samples of PS and PS/GO 1.0 wt. % were snapped frozen in Liquid Nitrogen and placed in the FC6 cryo chamber to equilibrate for around 30 minutes. Ultrathin sections, approximately 90-100nm thick, were cut using a Leica UC 6 ultra-microtome and FC6 cryo-box both manufactured by Leica Gmbh (Vienna, Austria) and supplied by Leica microsystems (Cambridge, UK). The cryo-box was attached onto uncoated 200 mesh copper grids at temperatures of between -60 to -100 °C. Sections were examined using a FEI Tecnai TEM at an accelerating voltage of 80 kV and 100 kV. Electron micrographs were recorded using a Gatan Orius 1000B digital camera and Gatan digital micrograph software. The camera and the related software were manufactured by (Gatan Inc. USA) and supplied by (Gatan, Abingdon, UK).

A Scanning Electron Microscopy (SEM Inspect F, Poland) was used to characterise the fracture surface for the samples using different magnification powers. Cryogenic fracture surfaces were obtained via snapping samples in liquid nitrogen. The neat polymer and the PS/GO 1.0 wt. % were soaked in a container of liquid nitrogen for 5 minutes and snapped inside the container to obtain a clean fracture surface.

A gold sputter coater (Emscope SC500, England) was used for coating the polymer and the nanocomposite fracture surfaces. Samples were mounted to the sample holder of 25 mm diameter, 16 mm height with doubled angle 90° made from aluminium manufactured by Agar scientific, Germany. Polymer and nanocomposite sample were coated manually with silver dag before coating them with gold using the sputter coater machine. Coating started when the vacuum inside the chamber was about 0.06 Tor. The current utilised for coating process was 15 mA and the time required for accomplishing coating process was 3 minutes apart of the time consumed to reach the required pressure inside the chamber which was about 10 minutes. GO powder was distributed over an aluminium pin stub of high purity and it was taken to SEM imaging after making gold coating only. There was no need for coating GO powder by silver dag.

Fourier Transform Infra-red Spectroscopy (FTIR Spectrum 100 Perkin Elmer, USA) which had a wavenumber coverage of range of 400-4000 cm⁻¹ was used for characterising graphite, graphite oxide, GO, PS and PS/GO nanocomposites. Accumulations was 16 scans. The used source attached to the machine was MIR 8000-30 cm⁻¹ and the detector was MIR TGS 15000-370 cm⁻¹. The scan speed was 0.2 cm/sec and the resolution was 4 cm⁻¹.

Raman spectra were recorded with equipping a CCD detector for graphite, GO, PS and the nanocomposites using the Reinshaw inVia Raman microscope, England.

The wavelength of the source was 514.5 nm argon-ion laser at a power of 20 mW and resolution of 1 cm^{-1} . To investigate the crystal structure of graphite, GO, PS and its nanocomposites D2 Phaser, X-ray diffraction analyser (Bruker, USA) was employed with Ni filter and Cu target.

The size of the slot was 1 mm, operating current 10 mA, operating voltage 30 kV and scanning range (2θ) was from °5 to ° 50. The time was 0.3 and the steps was 3700. The detector was Lynxeye (1 D mode) and the wavelength was 0.154 nm.

Thermal Gravimetric Analysis (TGA Pyris 1, Perkin Elmer, USA) was used to measure thermal degradation temperature. The atmosphere used in the test was N_2 and the heating rate was 10 °C/min. The range of temperature used with graphite, GO, PS and PS/GO nanocomposites was from 28 to 600 °C. The weight of each sample inside the pan was 5 mg except the weight of GO powder that was few milligrams.

Differential Scanning Calorimetry (DSC 6 Perkin Elmer, USA) was used to determine the value of the glass transition temperature (T_g) which is the temperature at which the polymer transforming from glassy state to rubbery state. 10 mg of each sample was placed in a sealed pan of aluminium with an empty sealed aluminium pan used as a reference. Aluminium was selected as a sample holder and as a reference as it has a high heat capacity over a range of temperatures. Both of the sample and the reference were placed

inside the machine and subjected to a nitrogen gas purge at a rate of 50 ml.min⁻¹. The range of temperature was ramped from 25 °C to 240 °C at a rate of 10 °C. min⁻¹.

Dynamic Mechanical Analysis (DMA Perkin Elmer, DMA 8000, USA) was used to find the storage modulus for the neat polymer and nanocomposites where strain was 0.5% (0.05 mm), the range of temperature was 40 - 130 °C, the heating rate was 3 °C/min. and the oscillatory frequency was 1 Hz. The deformation mode utilised in this test was single cantilever bending.

3. Results and discussion

A dilute and clear colloidal suspension of GO was obtained in distilled water. In order to overcome the attractive Vander Waal forces between the graphitic layers, liquid phase exfoliation was applied and assisted by mechanical exfoliation to obtain small graphene nano-particles that have lateral sizes up to 1 μ m. The use of liquid phase exfoliation generally, and sonication specifically leads to detrimental effects on the nano-sheets in terms of defect formation in the periphery of the sheets. However, the approach is still desirable and extensively applied because single layer GO sheets can be obtained and it is an environmentally friendly approach.^[7,18,19]

Figure 1 shows the dimensions of GO flakes. It confirms the thickness of the GO sheets varies between 0.7 and 1.1 nm and the lateral size varies between 863 nm to $1.2 \,\mu\text{m}$ for the different sheets. Some researchers^[20] had shown that the thickness of a monolayer GO nano-sheet is 1- 1.4 nm, whilst the thickness of a single layer of graphene is about 0.34 nm. The reason behind this variation can be attributed to the presence of adsorbed molecules and functional groups. The same authors elucidated the reasons behind the wide range of lateral sizes for the GO nano-sheets as follows: The multistep oxidation process for the large crystals of graphite increase the possibility of obtaining large GO sheets with lateral size up to 3 mm. A research group^[2] were identified another reason why GO sheet is thicker than graphene sheet. They suggested that it is due to the presence of covalently bound oxygen atoms. Furthermore, the slight displacement of SP³ hybridised carbon atoms above and below the original graphene plane also led to thickness differences.

Figure 2 refers to the relative even distribution of GO in the polymer matrix. The images that were taken by optical microscopy for the neat polymer film, and different



Figure 1. AFM image and the section analysis for the GO nano-sheets.



Figure 2. The OM images for the PS and the nanocomposites with different weight fractions.

concentrations of GO in the matrix, clarify the nature of nano-fillers distributed in the polymer. The optimum properties of the nanocomposites are only achievable with a homogeneous distribution for the nanofillers in the polymer matrix.

The performance of the nanocomposites is severely affected as the nano-scale reinforcements tend to coalesce into macro size agglomerates.^[21] Some authors^[22] had used OM to study the dispersion of carbon nanofibers in an epoxy matrix.

Figure 3a shows the IR of graphite, graphite oxide and GO. The sophisticated IR instruments are recording the data within the range of $400-4000 \text{ cm}^{-1}$. The spectrum of graphite does not display any peaks that appear in its oxidised forms.^[23] This result was confirmed in literature.^[24] For the graphite oxide and GO spectra, the effect of oxidation process is clearly recognised as the peaks are attributed to the presence of oxygen functional groups.

For the graphite oxide spectra, two main peaks can be found, the first one is the most prominent one that has a peak in 3286 cm^{-1} which is formed according to the C-OH stretching vibrations of the hydroxyl group. The other peak that can be seen for the graphite oxide is nearly at 1620 cm^{-1} which is formed due to C = C skeletal vibration for the graphite which is not oxidised.^[25] Some researchers^[24] were confirmed similar results for graphite oxide as they were reported a presence of broad peak located between 3000-3700 cm⁻¹due to free and adsorbed hydroxyl functional groups. They also reported the presence of peak that was located at 1620 cm⁻¹, and this peak was ascribed to the deformation vibration of adsorbed water molecules. The peaks of GO can be explained as: hydroxyl, epoxide and carboxylic acid groups and can be shown as a rich collection of absorption bands. The O-H stretching vibration can be seen in 3500 cm^{-1} . The other absorption peaks of C = O from the absorption of carbonyl and carboxylic acid groups,



Figure 3. a: IR spectra for graphite, graphite oxide, GO, PS and its nanocomposites. b: IR spectra for PS and its nanocomposites. The black dash lines are refer to PS, whereas the blue dash lines are refer to interaction between PS and GO.

C=C from the unoxidised graphitic domain, C – H and C – O from the absorption of epoxy groups can be seen at the wavenumbers (1720, 1450, 1340 and 1100) cm⁻¹ respectively. All of the vibrations are stretching vibrations apart from the C – H group which has a bending vibration.^[17,26] The literature was reported via some collaborators^[27] the presence of O-H, C=O, C=C, and epoxy C-O in their sample of GO.

Figure 3b shows the peaks related to PS which refer to = C-H aromatic stretching vibration in the range of $3100-3000 \text{ cm}^{-1}$. Asymmetric and symmetric stretching associated with vibration stretching of CH₂ can be noticed at peaks of 2929 cm⁻¹ and 2849 cm⁻¹ respectively. Peaks at 1600, 1580, 1491 cm⁻¹ are attributed to the stretching vibration of benzene ring. The C-H out of plane bending vibration of the benzene ring can be seen at 753 and 697 cm⁻¹.



Figure 4. a: The crystal structure for graphite and GO by Raman spectroscopy. b: Raman spectra for PS and its nanocomposites.

The weak shoulder at 1073 cm^{-1} confirms the interaction between PS and GO but a typical peak for GO cannot be found due to an overlap with PS peaks, or it is a weak peak.^[28] Co-authors^[26] were reported that the peak of 1023 cm^{-1} is another peak of interaction between PS and GO and the type of interaction is most likely to be Π - Π stacking.

Raman spectroscopy is a non-destructive technique for investigating the structure, electronic properties, doping level, defect structures and defect density of graphitic materials. It is also an efficient tool for characterising and analysing the order crystal structure of graphite's derivatives. The crystal structure for graphite and GO using Raman spectroscopy is shown in Figure 4a and b shows the crystal structure of PS and the nanocomposites. The G band is usually related to E_{2g} phonons by SP^{2} carbon atoms at 1575 cm^{-1} . The D band is associated with the breathing mode of k point photons of A_{1g} symmetry and this band is at 1350 cm⁻¹.^[29,30] These peaks referred to by the latter co-authors^[29,30] that are related to the G and D band were found in the current sample of graphite used in this research. The spectrum of graphite includes few Raman invisible active bands as it is a highly ordered material.

The weaker band (D band) in Figure 4a is caused by graphite edge defects, bond length disorder, bond angle disorder and vacancies. On the other hand, the sharp band (G band) appears due to in-phase vibrations of the graphitic lattice.^[31,32]

At around 2680 cm^{-1} , the D band has an overtone peak which is called the 2D peak. The shape and shift of this peak is intimately associated with the number of graphene layers and its position in the current graphite sample is appearing at around 2700 cm^{-1} . The reason for the appearance of this peak is due to the double resonance transitions resulting in the production of two photons with opposite momentum. Another important feature of this peak is that it is a clear and prominent peak even with the absence of defects in graphene sheet which is unlike the D band peak that is only active when defects are present.^[20]

Co-authors^[30] were confirmed the D and G band for graphite at 1594 cm^{-1} and 1358 cm^{-1} respectively with a clear 2 D peak at around 2700 cm^{-1} .

The oxidation process for the graphite caused a considerable change in the lattice structure of graphite due to the formation of oxygen functional groups at the edges and at the basal plane. It can be seen that the peak of the G band is shifted higher to 1589 cm^{-1} in accordance to the oxidation of graphite as a new SP³ carbon atom is formed in the graphitic lattice. In addition, the D band is shifted slightly higher (1357 cm^{-1}) and the intensity of the D band is also higher compared with its intensity in the graphite spectrum. These outcomes observed in GO can be attributed to the formation of disorder and defects such as aliphatic chain, grain boundaries and the presence of in-plane hetero-atoms. The oxidation reaction is behind the weakening or disappearance of the 2D peak as the stacking order is broken.^[32] The intensity ratio between the D band and G band (ID/IG) is used to evaluate the defective disorders or the graphitisation quality for the crystalline graphite. The significant increase for this ratio as compared with graphite from 0.092 to about 0.97 refers to the increase of disorder structure in the graphene sheet as a result of the oxidation process.^[33]

The literature reported by a research group^[34] confirmed the peaks of GO with a slight variation in the values of Raman shift and there was an increase in the ratio of (ID/ IG) for GO as compared with pristine graphite.

The Raman peaks of PS obtained by some collaborators^[35] are similar to what has been achieved for PS used in the current study. The C-H vibration is about $3000 \text{ cm}^{-1}(2900 \text{ and } 3052 \text{ cm}^{-1})$. Figure 4b shows Raman peaks for PS and nanocomposites. The carbon in the former is related to the aliphatic chain, but in the latter to the aromatic chain. About 800 cm^{-1} the low frequency C-C can be seen. At around 1600 cm^{-1} a strong C = C is noticed. The sharp peak at 1000 cm^{-1} is due to the aromatic carbon ring. As the loading fractions are very low, no shift can be seen for the Raman peaks of nanocomposites. The peaks of PS are still the prevailing peaks.

Some authors^[36] confirmed that the G band peaks of PS reinforced with Multi Wall Carbon Nano-Tubes MWCNT



Figure 5. XRD patterns of graphite, GO, PS and its nanocomposites.

are shifted to lower wavenumbers in (8.0 and 10.0) wt.% in spite of the identical shape of the peaks as compared with the sample that was reinforced with 6.0 wt.% and neat PS. The PS/MWCNT of 1.0 wt. % did not show any shift for any band.

Figure 5 shows the XRD patterns of graphite, GO, PS and the nanocomposites. It is worth mentioning here that some researchers are using XRD which is a powerful and efficient tool in characterising layered materials such as GO, and as a reliable provider for the completion of oxidation process.^[28,37]

The natural graphite peak shows a sharp characteristic peak at 2θ of 26.3° . This peak verifies the abundance of unoxidised graphite substances. A new peak is formed at 10.7° which indicates the disappearance of a sharp peak of graphite, reduction in graphite's crystal structure and formation of GO sheets which consequently refer to a successful oxidation process. These peaks for graphite and GO were found by a research group.^[38] Another research group^[39] found that the interlayer spacing was shifted higher from 0.33 nm for graphite to 0.81 nm for GO.

The same approach is found here as the interlayer spacing is going higher from 0.33 nm for graphite up to 0.82 nm for GO which confirms the accommodation of oxygen functional groups in the graphitic gallery that led to this result. The peaks of PS at 19.5° with the very broad and weak peak at 10° confirm the amorphous structure of PS.

The same peaks for PS were found by co-authors.^[40] For the nanocomposites, the only prominent peak is that related to PS and no obvious peak for GO can be found. This can be attributed to exfoliation of GO in the matrix with



Figure 6. SEM micro-graphs of cryogenic fractured surface for neat PS" top images" and PS/GO 1.0 wt. %.

random dispersion, and the decline in the peak intensity of GO is due to dilution of the polymer matrix and the broad peak of PS. For all of the aforementioned reasons, the periodic structure of GO could not be found in the XRD patterns of the nanocomposites.^[28,37,41]

Co-authors^[42] were reported that the incorporation for (0.5 and 1.0) wt. % of GO to PSF did not result in clear appearance for a peak related to GO in the XRD patterns for these nanocomposites. Instead a single broad peak was observed that indicated a factual change in the structure of the polymer which indicated the dispersion of GO in the amorphous structure of polysulfone.

Figure 6 shows SEM micrographs that clarify the morphology of the neat polymer and the 1.0 wt. % of GO reinforcing the polymer matrix. It can be concluded that the cryogenically fractured surface for PS is rough and uniform which is totally different to the micrographs of the nanocomposite where the roughness decreases with the incorporation of GO nano-particles. Aggregates of GO in a few random places can be seen in the morphology of the lower couple of images for the nanocomposites. Interesting findings were assured in the literature^[43] referred to the same approach for the morphology of the cryogenically fractured surface of PS and its nanocomposites that included different weight fractions of graphene nano-powder.

A research group^[44] obtained findings using SEM that referred to aggregations of graphene nano-platelets in a Polyurethane PU matrix with loading up to 2.0 wt. %.

In Figure 7a and b the thermal degradation behaviour is investigated for graphite, GO, PS and the nanocomposites.

No weight loss for graphite powder was observed even at high temperature (around 800 °C) because of the highly graphitised structure.^[45] Another study in the same year^[46] indicated the good thermal stability of graphite up to 800 °C. It can be noted for GO that it is thermally unstable due to significant mass reduction with increasing temperature.^[47] There is a gradual weight loss with the increment of temperature up to (170-180) °C and this rising weight loss is ascribed to the evaporation of water molecules in the GO structure. The major weight loss occurs at around 204 °C which is attributed to the decomposition of different kinds of oxygen functional groups in the structure of GO.^[48] This drastic weight loss is accompanied by the emission of H₂O and CO₂ gases as the main decomposed functional groups are hydroxyl and carboxylic functional groups

The third stage starts from around 350 °C up to 800 °C and here maximum weight loss appears which is around 60%. At this stage, the generation of CO gas is associated with the decomposition of carbonyl functional groups as a consequence of thermal treatment up to 500 °C.^[46] Some collaborators^[49] observed that the thermal degradation behaviour for GO includes two main steps, the 1st one is the mass loss up to 100 °C due to the removal of absorbed water, and the 2nd step occurred around 200 °C due to the decomposition of the oxygenated functional group. The thermal degradation temperature T_d for GO in the current



Figure 7. a: Thermal degradation behaviour for Graphite and GO. b: TGA curves for PS and its nanocomposites. The background figure is the DTG curves for GO, PS and its nanocomposites.

study is 224 °C. This is different to that found by some authors^[39] when they measure T_d for GO when it was found to be 161 °C. A possible explanation for the obtained result (high Td for the GO in the current study) is the abundance of functional groups that led to this high T_d temperature. On the other hand, the T_d temperature obtained by some co-authors^[34] is in accord with the current study.

For PS and nanocomposites shown in Figure 7b, it is clear that the incorporation of GO nano-sheets in the polymer matrix contribute positively in improving the thermal stability of the nanocomposites compared with pristine PS. It is clear there is a delay in onset decomposition for the PS/GO 1.0 wt. % compared with the neat PS.

The pristine PS starts to decompose at around 142°C and it is fully decomposed at around 450 °C. The main reason for the PS decomposition is the main chain pyrolysis.^[50] The T_d temperature gradually increases with increasing weight fraction addition to the polymer. This represents an improvement in thermal stability for the nanocomposites and can be attributed to the homogeneous distribution of the GO nanosheets in the matrix. This leads to a more efficient dissipation of heat throughout the polymer matrix, and better retardation in terms of thermal decomposition.^[51]



Figure 8. DMA curves for PS and the nanocomposites.

This behaviour was emphasised by a research group^[52] when they showed that the T_d temperature is increased for PS when it is reinforced with different weight fractions of functionalised GO (0.1, 0.5 and 1.0) wt. %. Here the improvement in thermal stability was successfully obtained for the PS nanocomposites under the influence of air and nitrogen atmosphere respectively. Hence, it could be conceivably demonstrated that the incorporation of low loadings of graphene or its derivatives or reductants into different polymer matrices may lead to improve thermal performance as confirmed by research groups.^[53,54]

Figure 8 illustrates the thermomechanical behaviour for the PS and its nanocomposites. It should be emphasised that the polymer and nanocomposites are in a glassy state at room temperature as the chains are frozen and motionless but they transform to the rubbery state as the temperature is raised.^[55]

The inverse relationship between temperature and storage modulus can be clearly seen. As the temperature increases, cooperative motion for the polymer chains occurs and this motion of the chains is accompanied by energy dissipation leading to a decrease in storage modulus. The former measures the stored energy, representing the elastic portion of the curve.

The second set of analyses discusses the assessment of the GO addition to the polymer in terms of storage modulus improvement. The storage modulus increases consistently with the addition of increasing weight fractions of GO to the neat polymer, consistent with an increase in the rigidity of the nanocomposites compared with the pristine polymer.

The restricted movement of the polymer chains, the larger aspect ratio of GO nanosheets, the higher modulus for GO nanosheets, the stronger interfacial interaction between the polymer and the nanofillers, and the homogeneous distribution of GO nanoparticles in the polymer matrix are the most important reasons for the consistent improvement of the thermomechanical performance for the nanocomposites compared with the neat polymer.^[39,41,45] Some collaborators^[56] were confirmed the same behaviour for the PS when it is reinforced with different very low weight fractions of graphene.



Figure 9. DSC curves for PS and nanocomposites.

Different findings compared to the literature had been reported by some authors^[36] when they highlighted the negative thermomechanical performance for the PS when it was reinforced with higher weight fractions of MWCNT. They highlighted a decrease in storage modulus for PS with the incorporation of 8.0 and 10.0 wt. % of MWCNT compared with 6.0 wt. % and other lower concentrations. The authors attributed this to the agglomeration of nanoparticles that led to poor interfacial interaction between the nanoparticles and polymer molecules.

Figure 9 shows the values of T_g that were recorded by the DSC measurements as part of this study. It can be seen that there is a slight increase in the values of the glass transition temperature T_g with increasing weight fraction of GO in the PS. This behaviour can be explained by the retardation of the molecular motion due to interaction with the GO nanosheets that have high surface area.

The observed increase in the values of Tg can be attributed to the fine dispersion of GO in the PS because several dispersive techniques have been employed. The large surface area of the nanosheets produced confinement in the polymer chains and this leads to a higher glass transition temperatures for the nanocomposites compared with the neat polymer.^[43] It is important to report that no surface treatment is carried out for the GO. Despite the fact that some SP2 network of graphite sheets is damaged by the process of oxidation, the residual hexagonal honeycomb lattice might form conjugations with the PS adding more confinement for the GO with the plate structure of PS segments. This will result in an improvement in the values of Tg for the nanocomposites higher than PS.^[41] A research group^[57] were reported the effect of low loadings of GO on the PS matrix, and they confirmed what has been observed in the current study. As the loading of GO increases from (0.3 to 2.0) wt. %, so the T_g increases which is a consequence of the strong interfacial interaction between the nanosheets and the polymer.

This strong interfacial interaction inhibits free mobility of the adsorbed polymer chains in the interface. The following table shows the improvement in thermal and thermo-mechanical properties for the nanocomposites compared to the

 Table 1. Thermal and thermo-mechanical properties of neat polymer and its nanocomposites.

Sample	Td / °C	Tg / °C	Storage modulus at 30 °C / GPa
PS	425.58	99.4	1.41
PS/GO 0.01 wt.%	426.90	100.6	1.56
PS/GO 0.05 wt.%	427.70	101.1	1.69
PS/GO 0.1 wt.%	427.90	101.2	2.0
PS/GO 0.25 wt.%	427.50	101.3	2.19
PS/GO 1.0 wt.%	428.70	102.2	2.23

neat polymer. As the weight fraction of GO going higher, the performance is improved (Table 1).

Figure 10 shows the spatial dispersion for GO nanosheets in the PS matrix as well as the morphology of the nanocomposite and the neat polymer.

The black sheets represent the nanosheets and the grey background are the results obtained with the polymer. In 1st couple of images and at higher magnifications, curved and partially peeled nanosheets can be seen which provide an impression of the morphology of the nanocomposite material. At the lower magnifications of 100 and 50 nm the individual and finely dispersed sheets can be seen in the matrix. No stacking or aggregations for the nanosheets of GO can be found in the PS matrix.

These findings are in line with the disseminated literature.^[57] In order to show the difference in morphology between the neat polymer and the nanocomposite, images for pristine PS were also recorded. Figure 10 shows a series of TEM images and it can be clearly seen from the bottom two that no interesting nanosheets or recognisable morphology for the nanofillers can be confirmed. The images look more like that of a neat polymer with no reinforcing GO nanosheets, and the prevailing style for the images is the traces of cryo-micro sectioning that are due to preparation of the samples for imaging using TEM.

4. Conclusions

In this study, different low loadings of GO were incorporated homogenously into a PS matrix and different structural, thermal properties were studied as well as the nanomechanical behaviour for the polymer, and the nanosheets imaged in the cryogenically fractured surface. The incorporation of low loadings of the GO led to improvement in thermal and thermomechanical performance as the results of TGA, DSC and DMA indicated. As the homogenous dispersion for the nanosheets in the polymer matrix is a prerequisite for a good performance, this kind of dispersion was verified via different microscopic techniques carried out in this study. These techniques included OM, SEM and TEM. According to the very low weight fractions used in this study, no sharp peaks of GO appeared in Raman spectroscopy for the nanocomposites. Weak shoulders appeared in FTIR diagram and tiny humps can be seen in the curves of XRD. These can be attributed to the low loadings of GO in the PS that led to dilution of GO in the polymer matrix. In general, the incorporation of GO in PS using low loadings led to improve thermal and thermomechanical



Figure 10. TEM micrographs of PS/GO 1.0 wt. % and pure PS.

performance for the nanocomposites compared to the neat polymer. T_d , T_g , and storage modulus were increased as the weight fraction of GO went higher.

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References

- Maheshkumar, K. V.; Krishnamurthy, K.; Sathishkumar, P.; Sahoo, S.; Uddin, E.; Pal, S. K.; Rajasekar, R. Research Updates on Graphene Oxide Based Polymeric Nanocomposites. *Polym. Compos.* 2014, 35, 2297–2310. DOI: 10.1002/pc.22899.
- [2] Nikolaeva, M. N.; Bugrov, A. N.; Bezrukova, M. A.; Rabchinskiic, M. K.; Dideikin, A. T. Reduced Graphene Oxide Resistance in Composites with Polystyrene of Different Molecular Masses. *Fullerenes, Nanotubes and Carbon Nanostruct.* **2021**, *11*, 1–5. DOI: 10.1080/1536383X.2019.1686628.
- [3] Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A. Graphene Filled -Polymer Nanocomposites. J. Mater. Chem. 2011, 21, 3301–3310. DOI: 10.1039/C0JM02708A.

- [4] Guo, S.; Dong, S. Graphene nanosheet: synthesis, molecular engineering, thin film, hybrids, and energy and analytical applications. Chem. Soc. Rev. 2011, 40, 2644–2672. DOI: 10.1039/ c0cs00079e.
- [5] Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-Based Composites. Chem. Soc. Rev. 2012, 41, 666–686. DOI: 10.1039/ c1cs15078b.
- [6] Sun, X.; Sun, H.; Li, H.; Peng, H. Developing Polymer Composite Materials: Carbon Nanotubes or Graphene? Adv. Mater. 2013, 25, 5153–5176. DOI: 10.1002/adma.201301926.
- [7] Andre Mkhoyan, K.; Contryman, A. W.; Silcox, J.; Stewart, D. A.; Eda, G.; |Mattevi, C.; Miller, S.; Chhowalla, M. Atomic and Electronic Structure of Graphene-Oxide. *Nano Lett.* 2009, 9, 1058–1063. DOI: 10.1021/nl8034256.
- [8] Liao, K.-H.; Mittal, A.; Bose, S.; Leighton, C.; Mkhoyan, K. A.; Macosko, C. W. Aqueous Only Route towards Graphene from Graphite Oxide. ACS Nano 2011, 5, 1253–1258. DOI: 10.1021/ nn1028967.
- [9] Gu, R.; Xu, W. Z.; Charpentier, P. A. Synthesis of Graphene Polystyrene Nanocomposites via RAFT Polymerization. *Polymer* 2014, 55, 5322–5331. DOI: 10.1016/j.polymer.2014.08.064.
- [10] Salavagione, H. J.; Martı nez, G.; Ellis, G. Graphene-Based Polymer Nanocomposites. In *Physics and Applications of Graphene - Experiments*, Mikhailov, S., Ed.; InTech, 2011. http://www.intechopen.com/books/physics-and-applications-of-graphene-experiments/graphene-based-polymer-nanocomposites.
- [11] Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R. E. Review Article: Polymer- Matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. J. Compos. Mater. 2006, 40, 1511–1577. DOI: 10.1177/0021998306067321.
- [12] Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Adv. Mater. 2010, 22, 3906–3924. DOI: 10.1002/adma.201001068.
- [13] Dhand, V.; Rhee, K. Y.; Ju Kim, H.; Ho Jung, D. A Comprehensive Review of Graphene Nanocomposites: Research Status and Trends. J. Nanomater. 2013, 2013, 1–15. DOI: 10. 1155/2013/763953.
- [14] Yuan, M.; Erdman, J.; Tang, C.; Ardebili, H. High Performance Solid Polymer Electrolyte with Graphene Oxide Nanosheets. *RSC Adv.* 2014, 4, 59637–59642. DOI: 10.1039/C4RA07919A.
- [15] Mohammadsalih, Z. G.; Inkson, B. J.; Chen, B. The Effect of Dispersion Condition on the Structure and Properties of Polystyrene/Graphene Oxide Nanocomposites. Polym. Compos. 2021, 42, 320–329. DOI: 10.1002/pc.25827.
- [16] Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. ACS Nano. 2010, 4, 4806–4814. DOI: 10.1021/nn1006368.
- [17] Ming, R.; Ding, Y.; Chang, F.; He, X.; Feng, J.; Wang, C.; Zhang, P. Humidity-Dependant Compression Properties of Graphene Oxide Foams Prepared by Freeze-Drying Technique. *Micro & Nano Lett.* **2013**, *8*, 66–67. DOI: 10.1049/mnl.2012. 0833.
- [18] Potts, J. R.; Dreyer B, D. R.; Bielawski, C. W.; Ruoff, R. S. Graphene-Based Polymer Nanocomposites. *Polymer* 2011, 52, 5–25. DOI: 10.1016/j.polymer.2010.11.042.
- [19] Economopoulos, S. P.; Tagmatarchis, N. Chemical Functionalization of Exfoliated Graphene. *Chemistry* 2013, 19, 12930–12936. DOI: 10.1002/chem.201302358.
- [20] Eda, G.; Chhowalla, M. Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics. Adv. Mater. 2010, 22, 2392–2415. DOI: 10.1002/adma. 200903689.
- [21] Paul, D. R.; Robeson, L. M. Polymer Nanotechnology: Nanocomposites. *Polymer* 2008, 49, 3187–3204. DOI: 10.1016/j. polymer.2008.04.017.
- [22] Prolongo, S. G.; Burón, M.; Gude, M. R.; Chaos-Morán, R.; Campo, M.; Ureña, A. Effects of Dispersion Techniques of Carbon Nanofibers on the Thermo-Physical Properties of

Epoxy Nanocomposites. Compos. Sci. Technol. **2008**, *68*, 2722–2730. DOI: 10.1016/j.compscitech.2008.05.015.

- [23] Suresh, I. K.; Chidambaram, K.; Vinod, V.; Rajender, N.; Venkateswara, R. M.; Miroslav, Č. Synthesis, Characterization and Optical Properties of Graphene Oxide Polystyrene Nanocomposites. *Polym. Adv. Technol.* 2015, *26*, 214–222. DOI: 10.1002/pat.3435.
- [24] Hontoria-Lucas, C.; Lopez-~Einado, A. J.; De Lopez-Gonzalez, J. D.; Rojas-Cervantes, M. L.; Mart~~Randa, R. M. Study of Oxygen-Containing Groups in a Series of Graphite Oxides: Physical and Chemical Characterization. *Carbon* 1995, 33, 1585–1592. DOI: 10.1016/0008-6223(95)00120-3.
- [25] Drewniak, S.; Muzyka, R.; Stolarczyk, A.; Pustelny, T.; Kotyczka-Morańska, M.; Setkiewicz, M. Studies of Reduced Graphene Oxide and Graphite Oxide in the Aspect of Their Possible Application in Gas Sensors. Sensors (Basel, Switzerland) 2016, 16, 103. DOI: 10.3390/s16010103.
- [26] Yin, G.; Zheng, Z.; Wang, H.; Du, Q.; Zhang, H. Preparation of Graphene Oxide Coated Polystyrene Microspheres by Pickering Emulsion Polymerization. J. Colloid Interface Sci. 2013, 394, 192–198. DOI: 10.1016/j.jcis.2012.11.024.
- [27] Xu, C.; Shi, X.; Ji, A.; Shi, L.; Zhou, C.; Cui, Y. Fabrication and Characteristics of Reduced Graphene Oxide Produced with Different Green Reductants. *PLoS One.* 2015, *10*, e0144842–15. DOI: 10.1371/journal.pone.0144842.
- [28] Han, Y.; Wu, Y.; Shen, M.; Huang, X.; Zhu, J.; Zhang, X. Preparation and Properties of Polystyrene Nanocomposites with Graphite Oxide and Graphene as Flame Retardants. J. Mater. Sci. 2013, 48, 4214–4222. DOI: 10.1007/s10853-013-7234-8.
- [29] Ma, Q.; Song, J.; Jin, C.; Li, Z.; Liu, J.; Meng, S.; Zhao, J.; Guo, Y. A Rapid and Easy Approach for the Reduction of Graphene Oxide by Formamidinesulfinic Acid. *Carbon* 2013, 54, 36–41. DOI: 10.1016/j.carbon.2012.10.067.
- [30] Liu, Y.; Zhang, Y.; Duan, L.; Zhang, W.; Su, M.; Sun, Z.; He, P. Polystyrene/Graphene Oxide Nanocomposites Synthesized via Pickering Polymerization. Prog. Org. Coat. 2016, 99, 23–31. DOI: 10.1016/j.porgcoat.2016.04.034.
- [31] Mohan, V. B.; Brown, R.; Jayaraman, K.; Bhattacharyya, D. Characterisation of Reduced Graphene Oxide: Effects of Reduction Variables on Electrical Conductivity. Mater. Sci. Eng, B. 2015, 193, 49-60. DOI: 10.1016/j.mseb.2014.11.002.
- [32] Krishnamoorthy, K.; Veerapandian, M.; Yun, K.; Kim, S.-J. The Chemical and Structural Analysis of Graphene Oxide with Different Degrees of Oxidation. *Carbon* 2013, 53, 38–49. DOI: 10.1016/j.carbon.2012.10.013.
- [33] Tang, Z.; Zhang, L.; Zeng, C.; Lin, T.; Guo, B. General Route to Graphene with Liquid-like Behaviour by Non-Covalent Modification. *Soft Matter* 2012, 8, 9214–9220. DOI: 10.1039/ c2sm26307f.
- [34] Tripathi, S. N.; Saini, P.; Gupta, D.; Choudhary, V. Electrical and Mechanical Properties of PMMA/Reduced Graphene Oxide Nanocomposites Prepared via in Situ Polymerization. J. Mater. Sci. 2013, 48, 6223–6232. DOI: 10.1007/s10853-013-7420-8.
- [35] Yan, X.; Itoh, T.; Kitahama, Y.; Suzuki, T.; Sato, H.; Miyake, T.; Ozaki, Y. A Raman Spectroscopy Study on Single-Wall Carbon Nanotube/Polystyrene Nanocomposites: Mechanical Compression Transferred from the Polymer to Single-Wall Carbon Nanotubes. J. Phys. Chem. C. 2012, 116, 17897–17903. DOI: 10.1021/jp303509g.
- [36] Srivastava, R. K.; Srivishnu Vemuru, V. M.; Zeng, Y.; Vajtai, R.; Nagarajaiah, S.; Ajayan, P. M.; Srivastava, A. The Strain Sensing and Thermal-Mechanical Behaviour of Flexible Multi-Walled Carbon Nanotube/Polystyrene Composite Films. *Carbon* 2011, 49, 3928–3936. DOI: 10.1016/j.carbon.2011.05.031.
- [37] Szabó, T;.; Berkesi, O.'; Forgó, P't.; Josepovits, K.; Sanakis, Y.; Petridis, D. DéKáNy, I. Evolution of Surface Functional Groups in a Series of Progressively Oxidized Graphite Oxides. *Chem. Mater.* 2006, 18, 2740–2749. DOI: 10.1021/cm060258+.
- [38] Zhang, H.-B.; Wang, J.-W.; Yan, Q.; Zheng, W.-G.; Chen, C.; Yu, Z.-Z. Vacuum-Assisted Synthesis of Graphene from

Thermal Exfoliation and Reduction of Graphite Oxide. J. Mater. Chem. 2011, 21, 5392–5397. DOI: 10.1039/c1jm10099h.

- [39] Yu, Y.-H.; Lin, Y.-Y.; Lin, C.-H.; Chan, C.-C.; Huang, Y.-C. High-Performance Polystyrene/Graphene-Based Nanocomposites with Excellent anti-Corrosion Properties. *Polym. Chem.* 2014, *5*, 535–550. DOI: 10.1039/C3PY00825H.
- [40] Qian, T.; Yu, C.; Wu, S.; Shen, J. Gold Nanoparticles Coated Polystyrene/Reduced Graphite Oxide Microspheres with Improved Dispersibility and Electrical Conductivity for Dopamine Detection. *Colloids Surf. B. Biointerfaces* 2013, 112, 310–314. DOI: 10.1016/j.colsurfb.2013.08.005.
- [41] Yang, J.; Huang, L.; Li, L.; Zhang, Y.; Chen, F.; Zhong, M. Preparation of Polystyrene/Graphene Oxide Composites and Their Supercritical Carbon Dioxide Foaming. J. Polym. Res. 2013, 20, 1–9. DOI: 10.1007/s10965-013-0173-x.
- [42] Ionita, M.; Madalina Pandele, A.; Crica, L.; Pilan, L. Improving the Thermal and Mechanical Properties of Polysulfone by Incorporation of Graphene Oxide. *Compos. Part B: Engin.* 2014, 59, 133–139. DOI: 10.1016/j.compositesb.2013.11.018.
- [43] Basu, S.; Singhi, M.; Satapathy, B. K.; Fahim, M. Dielectric, Electrical and Rheological Characterization of Graphene Filled Polystyrene Nanocomposites. *Polym. Compos.* 2013, 34, 2082–2093. DOI: 10.1002/pc.22617.
- [44] Yadav, S. K.; Cho, J. W. Functionalized Graphene Nanoplatelets for Enhanced Mechanical and Thermal Properties of Polyurethane Nanocomposites. Appl. Surf. Sci. 2013, 266, 360–367. DOI: 10.1016/j.apsusc.2012.12.028.
- [45] Tang, L.-C.; Wang, X.; Gong, L.-X.; Peng, K.; Zhao, L.; Chen, Q.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q. Creep and Recovery of Polystyrene Composites Filled with Graphene Additives. Compos. Sci. Technol. 2014, 91, 63–70. DOI: 10.1016/j.compscitech.2013.11.028.
- [46] El-Khodary, S. A.; El-Enany, G. M.; El-Okr, M.; Ibrahim, M. Preparation and Characterization of Microwave Reduced Graphite Oxide for High-Performance Supercapacitors. Electrochim. Acta 2014, 150, 269–278. DOI: 10.1016/j.electacta. 2014.10.134.
- [47] T.K, B. S.; Nair, A. B.; Abraham, B. T.; Beegum, P. M. S.; Thachil, E. T. Microwave Exfoliated Reduced Graphene Oxide Epoxy Nanocomposites for High Performance Applications. *Polymer* 2014, 55, 3614–3627. DOI: 10.1016/j.polymer.2014.05. 032.
- [48] Malas, A.; Das, C. K. Effect of Graphene Oxide on the Physical, Mechanical and Thermo-Mechanical Properties of Neoprene

and Chlorosulfonated Polyethylene Vulcanizates. *Compos. Part B: Engin.* **2015**, *79*, 639–648. DOI: 10.1016/j.compositesb.2015. 04.051.

- [49] Chen, W.; Yan, L.; Bangal, P. R. Preparation of Graphene by the Rapid and Mild Thermal Reduction of Graphene Oxide Induced by Microwaves. *Carbon* 2010, 48, 1146–1152. DOI: 10. 1016/j.carbon.2009.11.037.
- [50] Wu, N.; She, X.; Yang, D.; Wu, X.; Su, F.; Chen, Y. Synthesis of Network Reduced Graphene Oxide in Polystyrene Matrix by a Two-Step Reduction Method for Superior Conductivity of the Composite. J. Mater. Chem. 2012, 22, 17254–17261. DOI: 10. 1039/c2jm33114d.
- [51] Hassan, M.; Reddy, K. R.; Haque, E.; Minett, A. I.; Gomes, V. G. High-Yield Aqueous Phase Exfoliation of Graphene for Facile Nanocomposite Synthesis via Emulsion Polymerization. *J. Colloid Interface Sci.* 2013, 410, 43–51. DOI: 10.1016/j.jcis.2013. 08.006.
- [52] Qiu, S.; Hu, W.; Yu, B.; Yuan, B.; Zhu, Y.; Jiang, S.; Wang, B.; Song, L.; Hu, Y. Effect of Functionalized Graphene Oxide with Organophosphorus Oligomer on the Thermal and Mechanical Properties and Fire Safety of Polystyrene. *Ind. Eng. Chem. Res.* 2015, 54, 3309–3319. DOI: 10.1021/ie504511f.
- [53] Zhang, L.; Zhu, L.; Chen, Y. Fabrication of Carbon Nanotubes/ Polystyrene Nanocomposites via Pickering Emulsion Polymerization. *Fullerenes, Nanotubes and Carbon Nanostruct.* 2021, 1–4. DOI: 10.1080/1536383X.2021.1909000.
- [54] Sheng, X.; Xie, D.; Cai, W.; Zhang, X.; Zhong, L.; Zhang, H. In Situ Thermal Reduction of Graphene Nanosheets Based Poly(Methyl Methacrylate) Nanocomposites with Effective Reinforcements. *Ind. Eng. Chem. Res.* 2015, 54, 649–658. DOI: 10.1021/ie5035978.
- [55] Hasan, M.; Lee, M. Enhancement of the Thermo-Mechanical Properties and Efficacy of Mixing Technique in the Preparation of Graphene/PVC Nanocomposites Compared to Carbon Nanotubes/PVC. Progress Nat. Sci. 2014, 24, 579–587. DOI: 10. 1016/j.pnsc.2014.10.004.
- [56] Ren, P.-G.; Yan, D.-X.; Chen, T.; Zeng, B.-Q.; Li, Z.-M. Improved Properties of Highly Oriented Graphene Polymer Nanocomposites. J. Appl. Polym. Sci. 2011, 121, 3167–3174. DOI: 10.1002/app.33856.
- [57] Wan, C.; Chen, B. Reinforcement and Interphase of Polymer/ Graphene Oxide Nanocomposites. J. Mater. Chem. 2012, 22, 3637–3646. DOI: 10.1039/c2jm15062j.