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Effect of Reaction Time on the Synthesis of Graphene Oxide using Waste Tire

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Graphene oxide (GO) has been widely utilised in diverse applications due to its unique properties and versatile functionalisation capabilities. Maintaining the optimal synthesis parameters is crucial to producing high-quality GO with high oxidation. This study focuses on the effect of different reaction times during the modified Hummers method synthesis on the structural and morphological properties of GO derived from regenerated carbon black (CB) of waste tire. Using reaction times of 60, 120, and 180 minutes, the resulting GO samples were systematically examined through various characterisation techniques. FTIR spectroscopy confirmed the increased intensity of O-H bond vibrations, correlating with longer reaction times. XRD analysis revealed that increasing reaction times resulted in broader and more amorphous peaks, indicative of greater intercalation of oxygen-containing groups. Notably, as the reaction time increases, the oxygen content in the GO also increases, as evidenced by the intensified EDX peaks. Our findings demonstrate that the reaction time significantly influences the degree of oxidation and the distribution of functional groups in GO. This research provides valuable insights into the synthesis of GO from sustainable sources, promoting cost-effective and environmentally friendly approaches to advance material production.

Keywords: Graphene oxide; waste; tire; carbon black; reaction time

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Graphene oxide (GO) is a highly versatile material with unique properties that make it an essential component in various applications, including electronics [1], energy storage [2], water purification [3], and biomedical fields [4]. Unlike pristine graphene, GO contains oxygenated functional groups, such as hydroxyl, epoxy, and carboxyl, which enhance its solubility and facilitate further functionalization [5]. These properties make GO a promising candidate for various advanced technologies. The synthesis of high-quality GO with a high degree of oxidation is critical to maximizing its functional properties. GO with high oxygenated functional groups is favourable for use in healthcare settings due to its enhanced reactivity and potential for functionalization [6]. The modified Hummers method is one of the most widely used techniques for producing GO. Optimizing synthesis parameters, such as reaction time, is crucial as it significantly affects the structural and morphological properties of the resulting GO [7]. Reaction time influences the degree of oxidation and the distribution of oxygen-containing functional groups, which are pivotal for the material's performance in various applications. Despite its importance, limited research exists on the effect of reaction time on the quality of GO synthesized from carbon black (CB).

Apart from the synthesis process, the mass production of GO faces significant challenges due to the high cost of pure graphite, the primary raw material used in the process, contributing to the overall expense of manufacturing GO. Pure graphite obtained from mining is significantly more expensive, by at least one order of magnitude, than industrial graphite [8]. The demand for natural graphite has surged in recent years due to the expansion of end-user electronics markets, exerting considerable pressure on supply and value chains. Although global reserves and ore quality of natural graphite are high, mining operations need to be developed in many regions with mineral deposits. Malaysia, for instance, lacks natural graphite reserves, necessitating exports from major graphite-exporting countries such as China, Mozambique, and Madagascar [9]. This reliance on exports has driven up the price of graphite significantly.

The modified Hummers' method is one of the most widely used approaches to the synthesis of GO

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due to its simplicity and scalability. However, the quality and functionality of the resulting GO are highly dependent on the reaction parameters, including the reaction time. Previous studies show that the reaction time in the synthesis of GO in the modified Hummers' method significantly influences the degree of oxidation, exfoliation, and the distribution of oxygen functional groups within the carbon lattice. Despite this, limited studies have thoroughly examined the effect of reaction time on GO synthesized from alternative carbonaceous precursors. Previous researchers have mainly focused on graphite-based GO [10,11]. Aixart et al. (2021) examined how increased reaction time in the Hummers' method enhances exfoliation and reduces oxidation degree when using graphite as a precursor [12]. Similarly, Dziejarski et al. (2025) explored the chemical conversion and subsequent reduction of rCB into reduced graphene oxide (rGO) using long-duration oxidation and reductive treatments [13]. However, these studies emphasize either graphite-derived GO or the production of rGO, with limited emphasis on the evaluation of shorter reaction time effects on GO synthesis from rCB. Thus, this gap underscores the need for further studies into the oxidation behavior of GO from recovered carbon black of waste tire precursor, focusing on shorter reaction times.

Synthesized GO has diverse chemical functionalization based on epoxides, hydroxyls, carbonyls, and carboxyl groups. Severe pre-treatments influence these functionalities and must be addressed during the synthesis of GO. The presence of oxygenated groups on the surface of GO can be utilized to alter its characteristics and facilitate functionalization [14]. Controlling specific parameters during the synthesis process of GO allows for alteration of its electrical, optical, and mechanical properties. For example, highly oxygenated GO exhibits limited electrical conductivity but possesses exceptional antibacterial properties that are advantageous in medical healthcare applications [15]. Various modifications to the Hummers method have been used to improve the quality of GO by adjusting the oxidation degree of the samples through controlling the pre-treatment process. However, the vast range of possible changes has yet to be extensively explored, leaving room for further investigation on graphite oxidation and discrepancies between the obtained GOs.

For this purpose, this study proposed a novel study to utilize recovered carbon black (CB) from waste tires as an alternative carbon source to synthesize GO. The carbon black recovered from pyrolyzed waste tires (rCB) offers a promising feedstock for GO production. Despite its potential, there is limited published work on GO synthesis from rCB and a clear lack of understanding regarding the influence of shorter reaction time on the structural and chemical properties of such GO. Therefore, this study focuses on evaluating the effect of shorter reaction times (60, 120, and 180 minutes) on the morphology, oxidation level, and functional group content of GO synthesized from rCB. By highlighting the feasibility of synthesizing GO at shorter reaction times, this study contributes to both cost reduction and environmental sustainability in GO production.

EXPERIMENTAL

Materials

All chemicals used in this study were of analytical grade and utilized without further purification. Recovered carbon black (rCB) was obtained from Eco Power Synergy Sdn. Bhd with the carbon content ranging from 92-99 wt%. Concentrated sulphuric acid (H_2SO_4, 98%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Merck (Germany). Sodium nitrate ($NaNO_3$, ≥99%), potassium permanganate ($KMnO_4$, ≥99%), and hydrochloric acid (HCl, 37%) were obtained from Sigma-Aldrich (USA).

Synthesis of GO from Waste Tire

Graphene oxide was synthesised using the modified Hummers' method. The rCB was sieved to a particle size of 200 µm before use. One wt% rCB was added to a solution containing 23 mL of H_2SO_4, 1.0 g $NaNO_3$, and 3 wt% of CB, and the mixture was stirred in an ice bath for 2 hours. Subsequently, 3.0 g of $KMnO_4$ was gradually added to the mixture over 10 minutes. Next, the mixtures were allowed to react in varying reaction times (60, 120, and 180 minutes), and the temperature was maintained below 20°C in an ice bath. After removing the ice bath, the mixture was heated to 35°C for an hour. Then, 46 mL of distilled water was added, and stirring continued for 2 hours at 90°C. The reaction proceeded at room temperature with the addition of 100 mL of distilled water. To quench the oxidation reaction and remove excess $KMnO_4$, 10 mL of H_2O_2 was added slowly, followed by 1 hour of stirring. The mixture was washed with hydrochloric acid (HCl) and distilled water in a 1:3 ratio. Each washing cycle involved centrifugation at 8000 rpm for 5 minutes to separate the precipitate from the liquid, repeated until the solution reached a neutral pH. Finally, the GO samples were dried in an oven at 70°C for 24 hours.

Characterisation of GO

Raman spectroscopic measurements of the CB and GO samples were performed using a Raman microscope (Thermo Scientific model: DXR2xi). The spectra were acquired with a laser excitation wavelength of 532 nm and an integration time of 5.04 seconds. The XRD analysis is conducted using PANalytical X'pert PRO XRD diffraction (series number: DY2536), varying the 2θ from 5° to 90° at a scan speed of 2°/min. The FTIR analysis uses a Thermo Nicolet 6700 FTIR with an absorbance spectrum of 500-4000 cm^{-1}. The CB and the prepared samples were coated with a thin layer of gold-palladium (Au-Pd) to ensure the good electrical conductivity of the sample, allowing for precise and accurate imaging. Then, the surface morphology and elemental composition of the CB waste tire and GO samples were analyzed using field emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDX). In this experiment, the magnification of FESEM was used to observe the surface of GO at 40,000x. The particle size distribution of GO samples was determined using a Zetasizer Nano ZS, following probe sonication and filtration to ensure uniform dispersion. Measurements were conducted at 25°C in triplicate using dynamic light scattering under fixed optical parameters for accuracy and reproducibility.

RESULTS AND DISCUSSION

The Raman spectra of carbon black (CB) and graphene oxide (GO) samples are presented in Figure 1, with each spectrum representing the average of three measurements taken from different regions of a drop-cast sample. Raman spectroscopy is crucial for assessing sample quality in graphitic materials through three key bands: the D-band, G-band, and 2D-band [15]. The GO samples show a notable D-band shift from 1305 cm^{-1} (CB) to 1363 cm^{-1} (GO) and G-band shifts from 1546 cm^{-1} (CB) to 1585 cm^{-1} (GO). The D-band shift toward higher wavenumbers in GO aligns with the finding of Kudin et al. (2008), who reported that oxidation-induced structural strain and the disruption of π-conjugation by oxygenated functional groups caused increased vibration energy of the sp^2 domains [16]. This shift reflects a reduction in the average size of the aromatic domains and greater lattice distortion due to chemical functionalization. Similarly, the G-band upshift toward higher wavenumbers corresponds to the conversion of sp^2-hybridised carbon to sp^3 hybridization due to oxidative treatment from CB to GO. The I_D/I_G ratio, which reflects the degree of disorder in graphitic materials, increases with reaction time, rising from 0.80 in GO-60 to 0.84 in GO-120 and 0.87 in GO-180. This increase suggests that longer reaction times result in greater defect formation and more sp^3 domains due to the introduction of oxygen-containing functional groups. These findings are consistent with previous work, which observed a similar trend using graphite to synthesize graphene oxide, further confirming that prolonged oxidation enhances disorder and defect formation in graphitic structures [17].

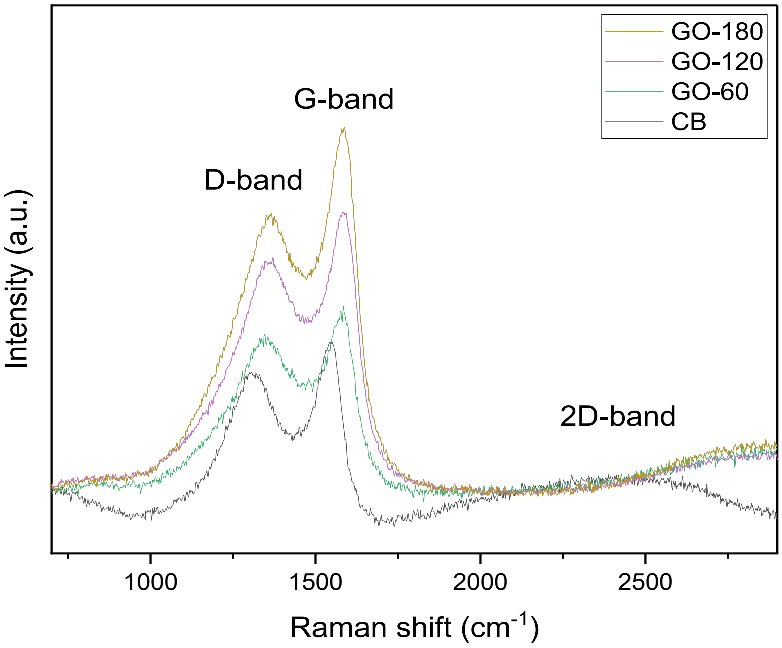


Figure 1. Raman spectra of the CB and GO prepared at different reaction times.

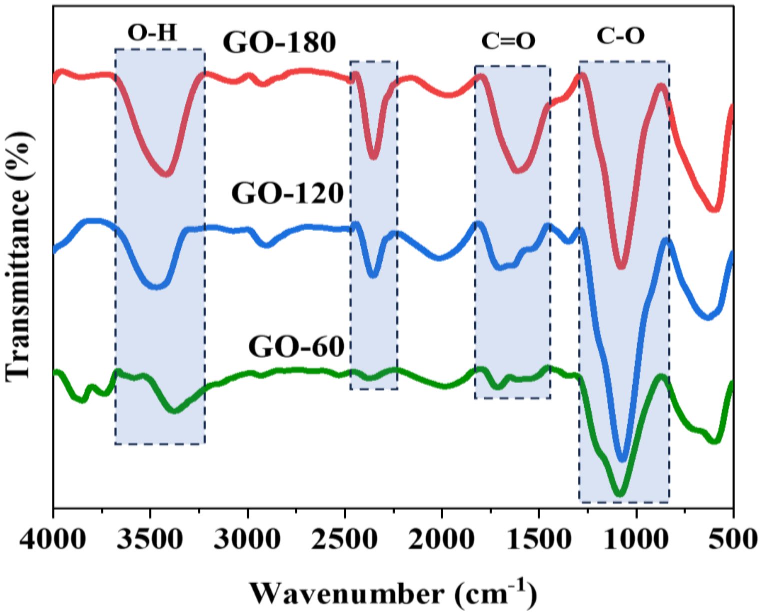


Figure 2. FTIR spectroscopy of GOs with different reaction times.

FTIR analysis is a powerful tool for determining the formation of oxygen-containing functional groups and the type of groups covalently grafted to the surfaces of GO samples as a result of oxidation [17]. Figure 2 shows that the FTIR spectra of GO treated with varying reaction durations of 60, 120, and 180 minutes are similar, with only minor changes in peak intensity. The peaks at 1720 cm^{-1} (C=O stretching) and within the range 1050–1250 cm^{-1} (C-O) stretching correspond to the formation of carbonyl and epoxy groups, respectively [18]. GO shows prominent peaks at 3400, 3500, and 3705 cm^{-1} for GO-60, GO-120, and GO-180, respectively. Interestingly, when the reaction period grows from 60 to 180 minutes, the stretching vibrations of O-H bonds increase significantly. This increase in peak intensity reflects a higher concentration of hydroxyl groups formed due to prolonged oxidation. The longer reaction time allows deeper penetration of oxidizing agents, facilitating greater functionalization of the graphene sheets with oxygen-based groups. The increasing intensity of these peaks is due to the enhanced oxidation, corroborating the hypothesis that extended reaction durations introduce more oxygen-containing groups.

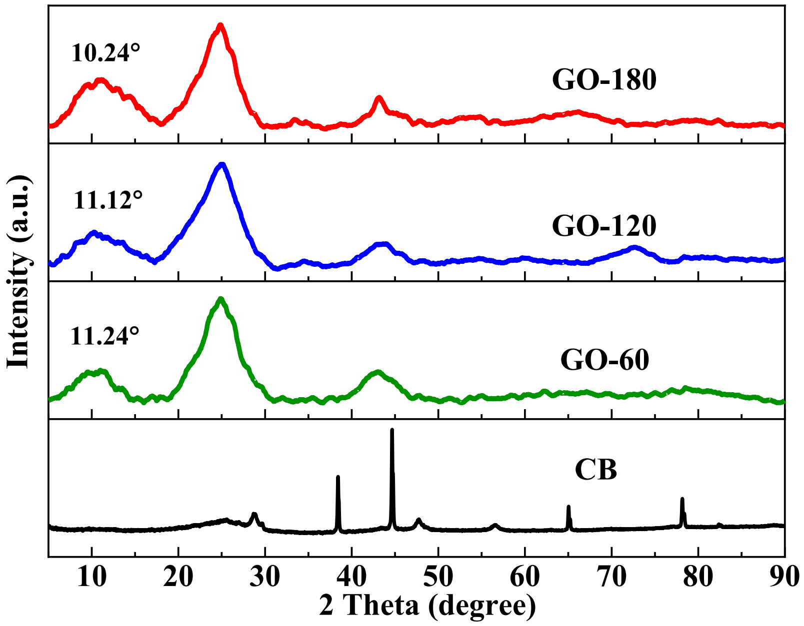
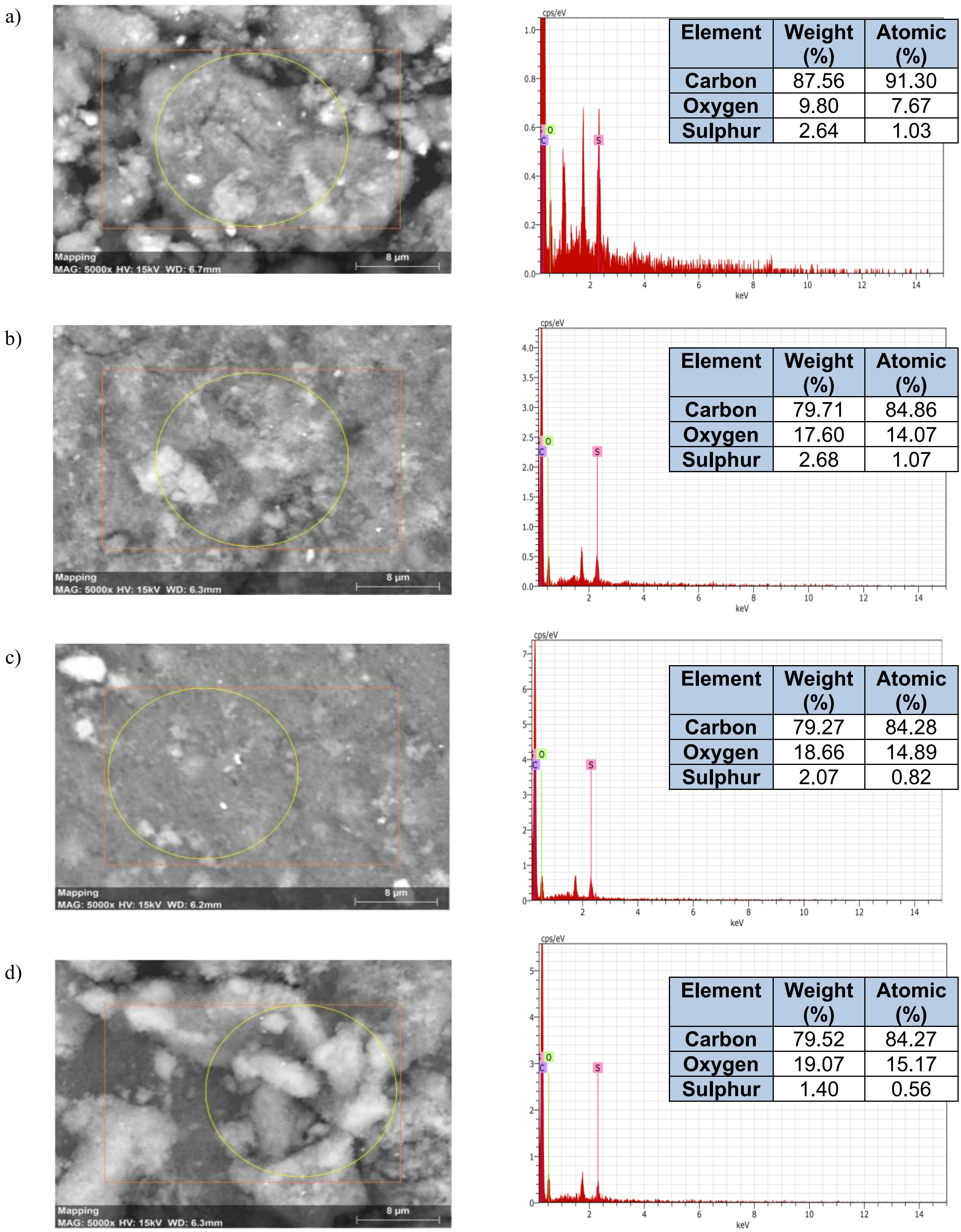


Figure 3. XRD spectra for CB, GO-60, GO-120 and GO-180 at different stages of reaction time.



a)

Element	Weight (%)	Atomic (%)
Carbon	87.56	91.30
Oxygen	9.80	7.67
Sulphur	2.64	1.03

b)

Element	Weight (%)	Atomic (%)
Carbon	79.71	84.86
Oxygen	17.60	14.07
Sulphur	2.68	1.07

c)

Element	Weight (%)	Atomic (%)
Carbon	79.27	84.28
Oxygen	18.66	14.89
Sulphur	2.07	0.82

d)

Element	Weight (%)	Atomic (%)
Carbon	79.52	84.27
Oxygen	19.07	15.17
Sulphur	1.40	0.56

Figure 4. GO sample EDX spectra showing the elements that were identified on (a) CB, (b) GO-60, (c) GO-120, and (d) GO-180.

Complementing the FTIR results, the XRD patterns in Figure 3 illustrate the structural evolution of GO. All GO samples exhibit a distinct peak at 2θ=26° in their XRD pattern, attributed to the (002) plane of carbon atoms, underscoring the presence of non-oxidized forms of CB [19]. However, with increased reaction time, another significant peak appears at a lower diffraction angle, confirming the successful oxidation of carbon to GO. The X-ray diffraction (XRD) analysis of samples GO-60, GO-120, and GO-180 at various reaction times revealed the presence of GO peaks at 2θ values of 11.24°, 11.12°, and 10.24°, respectively. The interlayer spacing of these samples was measured to be approximately 0.79, 0.82, and 0.87 nm, respectively. As the reaction time increased, the XRD pattern of the synthesized samples exhibited noticeable alterations in the phase of GO. Specifically, the intensity and broadness of the peak increased with reaction time. This broadening is due to the intercalation of oxygen-containing groups on the surface and basal planes of the GO during oxidation, causing the GO to appear in an amorphous phase rather than crystalline [20]. Notably, the peak for GO-180 is the most intense, indicating the highest degree of intercalation of oxygen-containing groups. The persistent peak at 2θ ≈ 26° for all three GO samples suggests the presence of some residual non-oxidized carbon, which indicates incomplete oxidation of the carbon black [21,22]. The FTIR and XRD peak changes further confirmed that prolonged reaction time leads to increased oxidation with enhanced incorporation of oxygen functionalities onto the layers of carbon.

Figure 4 displays the EDX spectra for CB and GO samples. The EDX mapping revealed that the GO samples mainly comprised carbon and oxygen. The spectrum displays a prominent peak for carbon, signifying its prevalence in the sample with 87.56 wt.% and 91.30 at.%. The oxygen content is 9.80 wt.% and 7.67 at. %, whereas sulphur has the lowest concentration at 2.64 wt.% and 1.03 at.%. Spectrum b) has a prominent peak for carbon, with a measurement of 79.71 wt.% and 84.86 at. %, respectively. The concentration of oxygen has risen to 17.60 wt.% and 14.07 at. %, while sulphur is at 2.68 wt.% and 1.07 at.%. Spectrum c) demonstrates the pattern by exhibiting carbon at 79.27 wt.% and 84.28 at. %, while oxygen is slightly higher than spectrum b) at 18.66 wt.% and 14.89 at.%. The sulphur content is 2.07 wt.% and 0.82 at.%. Spectrum d) displays carbon with 79.52 wt.% and 84.27 at. %, oxygen has climbed to 19.07 wt.% and 15.17 at. %, and sulphur is at its lowest point in the series with a weight percentage of 1.40 wt.% and an atomic percentage of 0.56 at.%. The variation of the oxygen content for all three samples demonstrated that the increased reaction time increases oxygen content in GO samples [19]. This phenomenon was correlated with the increment of oxygen contents to show that the formation of GO is successful due to the introduction of oxygen towards carbon-based material, which aligns with the FTIR results.

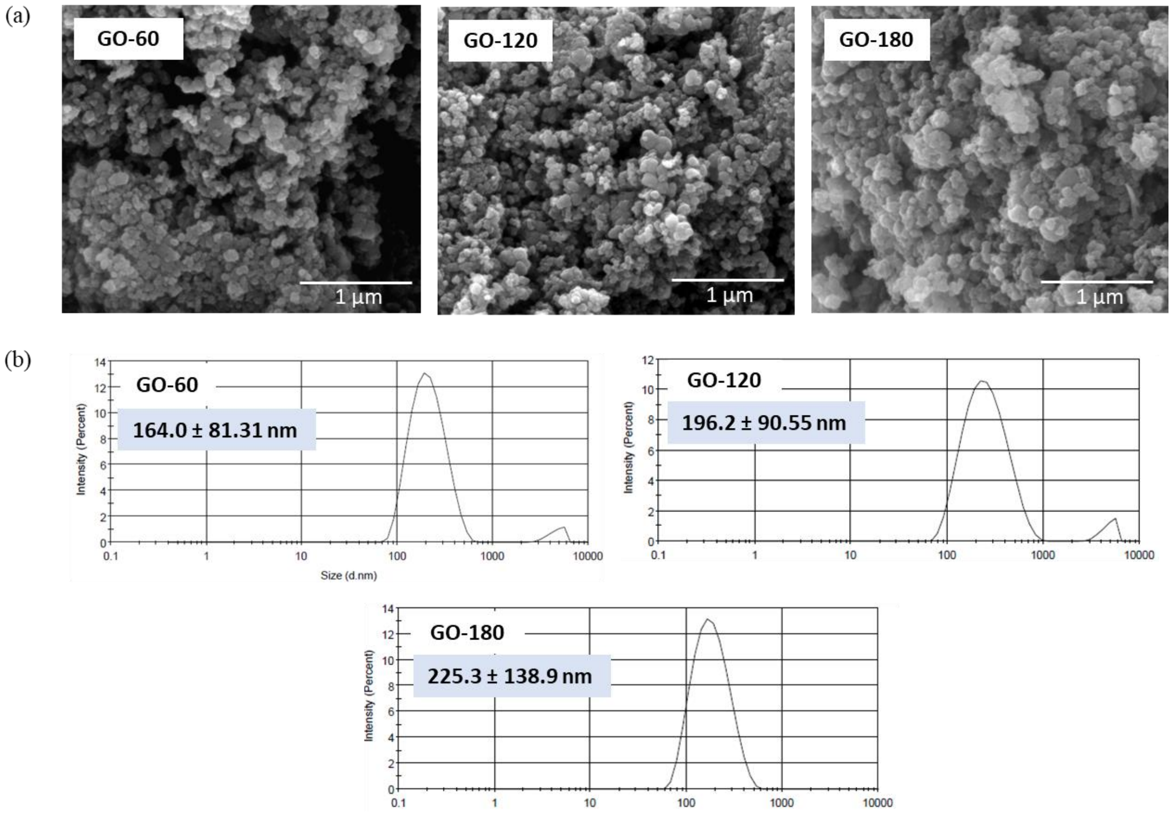


Figure 5.(a) FESEM images with magnification of 40000X and (b) Intensity-based particle size distribution of graphene oxide at different reaction times.

Figure 5 presents the FESEM images of GO samples at varying reaction times. The FESEM images (Figure 5a) shows that GO-60 exhibits well-dispersed and less agglomerated particles, suggesting that a shorter oxidation time resulted in limited disruption of graphitic layers. In contrast, GO-120 begins to show more agglomeration, while GO-180 displays larger and more compact clusters observed at higher magnifications. This morphological trend corresponds with the intensity-based particle size distribution analysis (Figure 5b), which shows an increased average particle size with longer reaction times. The increase in particle size is due to the excessive oxidation and structural damage that may promote the re-stacking and agglomeration of exfoliated particles. The increased oxidation introduces more oxygen-containing functional groups, leading to GO particle clustering [20]. Additionally, the unique composition of CB, derived from waste tires, contributes to the GO samples' diverse morphology and particle distribution, in contrast to graphite-based GO [21].

CONCLUSION

The present study offers a novel perspective on the scalable production methods for chemically modified GO generated from rCB derived from waste tires using a modified Hummers' method, with control durations of 60-180 minutes. Structural and morphological analyses confirmed that reaction time plays a critical role in tuning the physicochemical properties of GO. FTIR spectroscopy revealed increasing intensity of O-H, C=O, and C-O functional group peaks with longer reaction durations, indicating increased oxidation and enhanced incorporation of oxygen-containing groups. XRD analysis showed a shift in the (001) peak from 11.24° (GO-60) to 10.24° (GO-180), with corresponding increases in interlayer spacing from 0.79 nm to 0.87 nm, suggesting greater exfoliation and functional group intercalation. Raman spectra confirmed the oxidation of rCB to GO, with an increasing I_D/I_G ratio (from 0.80 to 0.87), reflecting a higher degree of structural disorder and defect density in GO with extended oxidation. FESEM images revealed more pronounced agglomeration and larger particle sizes at higher reaction times, correlating with intensity-based particle size distribution data. Additionally, EDX analysis indicated an increasing oxygen-to-carbon atomic ratio from GO-60 to GO-180, confirming enhanced surface oxidation. These combined physicochemical results confirm that reaction time is critical in tailoring the oxidation level, structural properties, and surface chemistry of GO synthesized from waste-derived precursors. The ability to modulate these characteristics provides a pathway to optimizing GO for specific functional applications in electronics, filtration, and antibacterial textiles, making this approach promising for sustainable and value-added reuse of waste tires.

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