



## Boosting poly(vinyl chloride) with waste-based plasticizer and green nanofiller

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### Abstract

Utilization of recycled polymers and solid waste into useful products is targeted for controlling greenhouse gas emissions. The aim is to prepare and apply novel and boosted environmentally friendly composites as full waste-based sources based on recycled polyvinyl chloride (PVC) matrix, waste-based plasticizer (P), and green  $\text{CaCO}_3$  nanofiller (F). Respectively, P and F improvers were obtained via the glycolysis of polyethylene terephthalate (PET) waste and from eggshells solid waste. Selected concentrations of composites were extruded and then hot-pressed. FTIR, XRD, and DLS data affirm the formation of amorphous P and crystalline F nanoparticles. PVC-F nanocomposites provide thermal stability; however, PVC-P specimens have a lower thermal profile due to plasticization. The results of the migration test indicate the stability of the proposed composites in different media. The surface hardness increased by adding more percentages of F nanofiller, by 28.6%, for PVC-F30; however, the addition of P decreased the hardness owing to the smooth plasticized surface. All concentrations of PVC-F nanocomposites promoted sharply the tensile strength of PVC; they also increased the elastic modulus by 82%. In addition, the PVC-P composites succeeded in increasing the strain to 46%. The proposed composite was applied as water pipes for the first time without failure, compared to neat recycled PVC. The given data approves the successful grafting of recycled PVC with waste-based polyester plasticizer and green carbonate nanofiller.

Keywords: recycled PVC;  $\text{CaCO}_3$  nanoparticles; plasticization; mechanical properties.

### 1. Introduction

Polyvinyl chloride (PVC) is considered as one of the most widely applied thermoplastic polymers that puts the sharply increased demands in the global markets [1,2]. PVC is characterized by the high strength, thermal stability, moisture and bacterial resistance, stability to migration, and stiffness. Like mentioned characteristics make PVC as a durable polymer compared with other famous thermoplastics, such as polypropylene and polyethylene. In addition, the presence of C-Cl group in PVC increases the possibility of the polymer backbone to attach with other materials for supporting more features, depending upon the field of application [3-5]. PVC and its composites are being used in many different industries and applications, such as water pipe, food packaging, cable and wire insulation, laminations, floor coverings, partition frames, synthetic clothing, in addition to the utilization as supporting materials in construction and infrastructural applications [6-8]. Some biological uses, and medical tools and devices are currently manufactured based on concentrations of PVC; drug packing, blood bags and hospital flooring are examples for the related application [9-11]. Focusing on the conversion of polymeric and solid waste to economic value, some trials for recycling were developed by means of chemical methods, such as homogeneous and heterogeneous catalysis, ionic liquids mediation, and super fluids. Other ways of physical and thermal recycling were reported depending on the process, matrix type, and formulation [12-17]. In fact, the base of recycling, and the exploitation of plastic waste, solid and industrial aggregates, nature-based materials, low-carbon reactants etc. are environmentally encouraged for potential and sustainable uses [18-23]. Some bio-based fillers, such as biochar and starch, have been utilized for the safe application of a wide range of polymers [24,25]. For recycling of PVC, the PVC-polyurea-isocyanurate network mixture was depolymerized via different glycolysis conditions including time, temperature and catalyst. The recycled PVC, obtained as ~90%, was found to have suitable degradation and viscosity to reuse in the injection molding processing [26]. Other thermoplastic polymer was recycled and then used as plasticizing filler for PVC [27]. Furthermore, it is well-known that PVC is usually subjected to plasticization process for easy formulation and application throughout different plasticizers. Generally, some plasticizing agents are being incorporated to PVC types for the purpose of smoothing, softening, and strain-gain [28]. As the added fillers directly affect the processing technique, in addition to the polymer type itself, so the plasticizers and fillers should be compatible with the selected formulation technique [29,30]. A series of plasticizer copolymers were applied to PVC, and optimized giving the best mechanical and physical performance, compared with the traditional types [31]. Another diester plasticizer was prepared from lactic acid, and then blended with PVC via a suitable processing technique. The results indicated good stability, compatibility and flexibility with reducing the glass transition temperature [32]. Another study discussed the effect of different stabilizers on the polyester-plasticized PVC composites for stable optical applications [33]. Different concentrations of dioctyl phthalate and triethyl citrate plasticizing fillers were adjusted for PVC; they altered the overall thermal

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profile and the migration properties [34]. A novel plasticizing compound derived from chlorinated paraffin and di(2-ethylhexyl) 4-hydrophthalate has exhibited more plasticizing efficiency and enhanced compatibility, compared with the commercial one [35]. Yu and Selvadurai examined the stability of plasticized PVC sheets after exposure to water and ethanol solutions with different concentrations [36]. Plasticized PVC with cardanol additive was prepared successfully, and compared with the commercial dioctyl terephthalate and epoxidated soybean oil; the results indicated more plasticizing effect, durability and UV/thermal stability using the first additive [37]. The properties of plasticizing effect, physical properties and mechanical performance of different ester plasticizers with different loading percentages on the flexibility of PVC matrix have been studied in details [38-40]. With definite applications, the thermoplastics need to be filled especially if they in the plasticized form. The  $\text{CaCO}_3$  is recommended for PVC because of its low-cost and the provided functionality. The induced increase in viscosity could be controlled by the softening and elasticity provided by the plasticizer itself. So the final properties are expected to be promoted. Based on the ideas given above, the research conducted on reinforcing PVC with full environmental materials is still inadequate, to the best of our knowledge. The objective of this research is to enhance recycled PVC with plasticizer obtained from recycled PET, and carbonate nanoparticles obtained from natural sources. Aligning with the international objective of recycling and reducing greenhouse gas emissions, the novelty arises from the complete waste source of the proposed composite. The obtained nanocomposites were applied as sustainable water pipes. The environmentally friendly fillers and composites were investigated by means of structural, thermal, physical, and mechanical characteristics.

## 2. Experimental and methods

### 2.1. Materials

The starting materials used are mentioned here. Ethanol and diethylene glycol (Fisher Scientific) were used for the glycolysis reaction. The recycled water bottles were used as the source of PET polymer. Zinc acetate and succinic acid (Fisher Scientific) were taken as catalytic agents. The eggshells waste was used for the source of green  $\text{CaCO}_3$  nanoparticles. All materials have been used as revived, excepting the waste materials exposed to washing.

### 2.2. Preparation of waste-based plasticizer and nanofiller

This section provides informative details on the formation of the waste-based plasticizer and green nanofiller. The proposed plasticizer was prepared using waste PET and glycol via glycolysis reaction as following. The post-consumed PET water bottles were cut with a crusher to small pieces with dimensions of  $2 \times 2 \text{ cm}^2$ . The crushed pieces were washed with water/ethanol solution, and then with distilled water, and dried at  $40^\circ\text{C}$  for two hours. The preparation process of waste-based plasticizer was performed by extrusion using a DP-Dongguan single-screw extruder. Firstly, the clean recycled PET pieces were included with diethylene glycol in the inputting position with a rotation speed of 28 rpm, and an internal pressure of 18 MPa. The extrusion temperature was elevated gradually, starting from the feeding zone to the extrudate zone, from  $210^\circ\text{C}$  to  $255^\circ\text{C}$ . 50 g PET, 40 ml diethylene glycol, 2 g zinc acetate and 10 g succinic acid were used at starting materials. The extrudate was cooled and crushed in the form of pellets to obtain the waste-based plasticizer (P). The environmentally friendly  $\text{CaCO}_3$  nanoparticles were prepared, as stated elsewhere [41], from the eggshells waste. The solid waste was collected, grinded, washed several times with hot water, and partially calcinated at  $\sim 400^\circ\text{C}$  for seven hours to obtain the carbonate/oxide intermix. The obtained nanoparticles were utilized as the green nanofiller (F) for improving the recycled PVC matrix.

### 2.3. Processing of PVC-waste-based plasticizer/ $\text{CaCO}_3$ nanocomposite

The processing of the proposed nanocomposites, regarding filling PVC matrix with waste-based plasticizer (P) and environmentally friendly  $\text{CaCO}_3$  nanofiller (F) particles, was performed by the same single screw extruder, as second extrusion for complete compatibility. The concentrations of P and F were adjusted from 0% to 7% and 40%, respectively. Firstly, the all components were fed and then the final nanocomposites were granulated in the form of pellets. The nanocomposites were finally subjected to hot-press, at 0.45 MPa and  $145^\circ\text{C}$ , to obtain the sheets of PVC-waste-based plasticizer/ $\text{CaCO}_3$  nanocomposites, which are labeled as PVC-P-F. The hot-press method was chosen for formulating the prepared composite in the shape of testing specimens. The obtained compressed sheets were then characterized. Such methodology assures the compatibility and distribution of fillers in the PVC matrix. The details of related concentrations of PVC-P-F nanocomposites are shown in the section of discussion.

### 2.4. Analysis and characterization

The spectra of Fourier transform infrared (FTIR) were measured by Bruker-Vertex FTIR spectrophotometer, the chemical structure was detected within the wavenumber range of  $400 \text{ cm}^{-1}$  and  $4000 \text{ cm}^{-1}$ . The X-ray diffraction patterns (XRD) were measured by the Bruker-Phaser XRD diffractometer using the XR source of CuK-alpha,  $1.54 \text{ \AA}$  wavelength, current of 50 mA, at 4K voltage within the range of  $5^\circ$  and  $70^\circ$ . The particle size distributions was identified by the Malvern NANO-ZS dynamic light scattering (DLS) using the sonication-bath at room temperature. The thermal stability was tested by thermogravimetric analysis (TGA) using Mettler Toledo SF-TGA analyzer; the samples were weighted throughout heating from the room temperature to 600 at  $\text{N}_2$  atmosphere with the rate of  $5^\circ\text{C}/\text{minute}$ . The Barcol impressor (Gardco) was used for determining the surface hardness according to the ASTM D-2583 standard. The tensile properties were measured by the Universal Tensile Tester following ASTM D-638 standard. The migration test was performed to the prepared composites following the standard of ASTM D-1239 within different environments.

### 3. Results and discussion

#### 3.1. Microstructural characterization

The structures of the prepared materials were investigated by Fourier transform infrared (FTIR). Figure 1 displays the formation of waste-based plasticizer. Specifically, the absorption band at  $2950\text{ cm}^{-1}$  is attributed to the C-H vibration stretching in  $\text{CH}_2$  groups. The band near  $1420\text{ cm}^{-1}$  characterizes the C-H vibration bending. The sharp band at  $1740\text{ cm}^{-1}$  is arising from the stretching of the more C=O groups in the prepared ester [42]. The further screened bands in the range of  $1070\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  are related to the C-O-C asymmetric and symmetric stretching in the polyester linkage [43]. In addition, the prepared green  $\text{CaCO}_3$  nanoparticles were characterized by FTIR as represented in Figure 2. The absorption broad band at  $1426\text{ cm}^{-1}$ , and the small one at  $880\text{ cm}^{-1}$  are attributed to the asymmetric stretching and bending vibrations of C-O bonds in  $\text{CaCO}_3$  [44-45]. The X-ray diffraction patterns (XRD) of waste-based plasticizer is shown in Figure 3; the wide diffraction peak located in the  $2\theta$  range of  $10^\circ$  and  $21^\circ$  characterizes the amorphous polyester phase. In that way; the formation of polyester plasticizer from the thermoplastic solid waste through the esterification is available. Similar results were reported elsewhere [46,47]. The XRD patterns confirm the obtaining of P, as given by the FTIR data. The formation of green  $\text{CaCO}_3$  nanoparticles was also confirmed by XRD analysis. As illustrated in Figure 4, the crystalline phase of calcium carbonate nanoparticles is reached regarding the presence of the main sharp peak at  $\sim 29.2^\circ$ , and the other shoulders at position degrees within the range of  $23^\circ$  and  $66^\circ$  [48,49]. Furthermore, the dynamic light scattering (DLS) characteristic technique (Figure 5) has confirmed the successful attaining of  $\text{CaCO}_3$  nanoparticles with an average particle size of 95 nm. The performed microstructural and sizing characterizations affirm the formation of the waste-based plasticizer and the calcium carbonate nanoparticles, which will be taken as environmentally friendly improvers for the recycled PVC matrix.

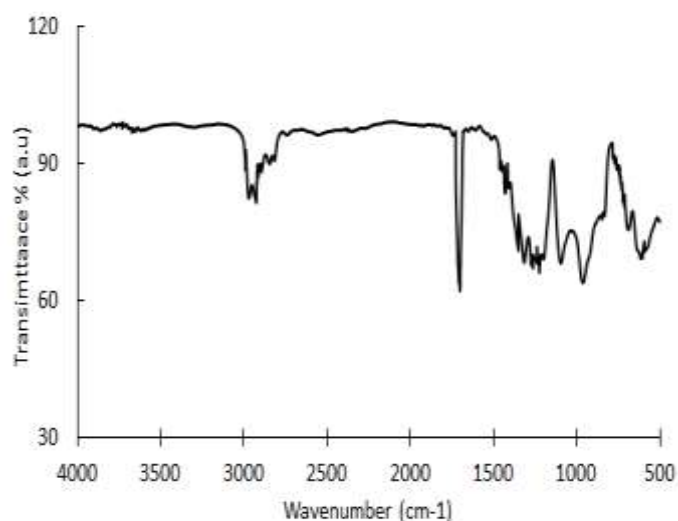


Figure 1: FTIR of waste-based plasticizer.

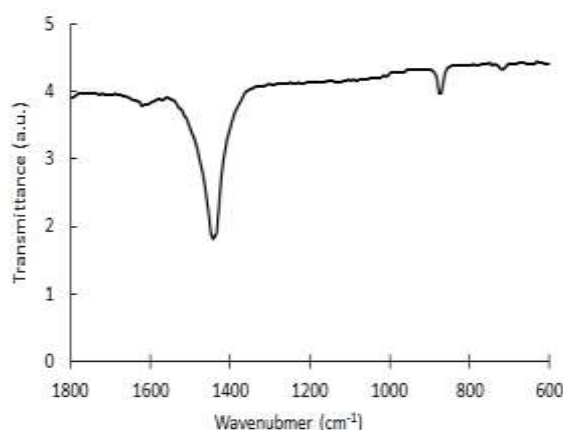


Figure 2: FTIR of green  $\text{CaCO}_3$  nanoparticles.

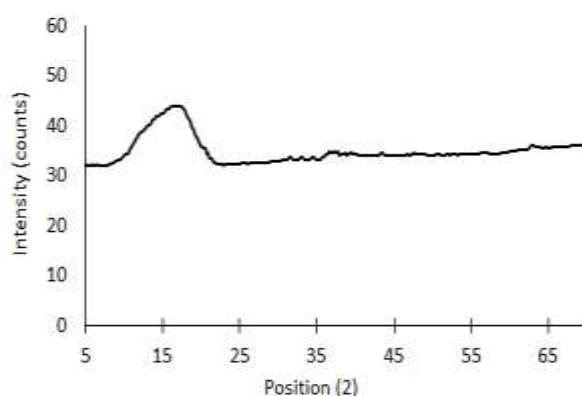
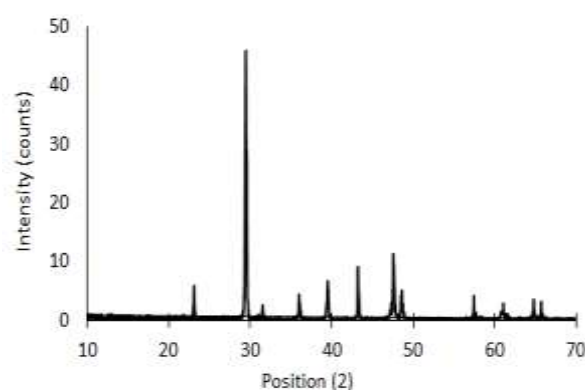
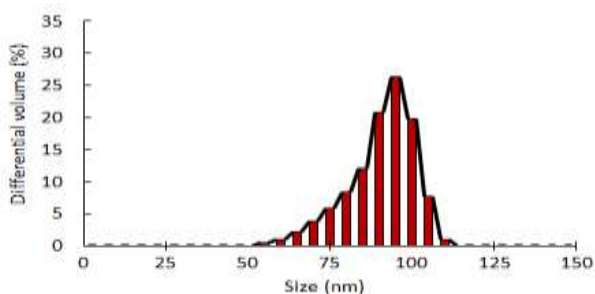


Figure 3: XRD of waste-based plasticizer.

Figure 4: XRD of green CaCO<sub>3</sub> nanoparticles.Figure 5: Particle size distribution of green CaCO<sub>3</sub> nanoparticles.

### 3.2. Thermal profile

As thermogravimetric analysis (TGA) is a standard testing in which the changes in mass-loss of a specimen is monitored during its progressive heating, the effects of grafting of the prepared P and F fillers on the thermal behavior of PVC matrix are studied by TGA. The related results of PVC-waste-based plasticizer composites are shown in Figure 6. As per the thermograms of neat PVC and its plasticized specimens, we notice a similar behavior corresponding to four fundamental zones of thermal decomposition. The first is an initial zone, which is located from the starting temperature to ~120 °C. It results from the standard dehydration process for the inside moisture content (evaporation of moisture and volatile impurities). The second zone, starting from ~180 °C to ~280 °C, represents the cleavage of backbone chains of PVC matrix. There is somewhat stable behavior after the second zone till ~350 °C, which possesses a lower rate of thermal decomposition. The temperature range between ~360 °C and ~420 °C is the third zone where all composites degrade sharply regarding the formation of char. With further ignition, the final zone appears to be a steady one, and accompanied with the residual content of ash. The specimens of PVC, which are filled by P show lower thermal stability compared with the neat PVC. The plasticization itself might smooth the flowability and increase the mobility and space among polymer segments, which may improve the mixing with numerous additives as spacer, however a decline in thermal behavior and other properties may be occur [50,51]. The low concentrations of the prepared plasticizer have a minimal effect on the thermal stability of PVC as noted by shifting the degradation temperatures to few lower

ones. PVC-P3 and PVC-P5 have acceptable stability near PVC; however the PVC-P7 has a noticeable low thermal stability. The obtained data are summarized in Table 1, it can be seen that the temperature of initial degradation due to 10% weight loss ( $T_{\text{onset}}$ ) located in the range of 204 °C and 200 °C for PVC-P3 and PVC-P5, however it recorded 191 °C for PVC-P7. This is similar to the temperatures of the main degradation at 50% weight loss ( $T_{0.50}$ ). The residual contents after ignition (R%) are almost the same due to the thermal degradation of organic materials. The TGA of PVC-green  $\text{CaCO}_3$  nanocomposites is indicated in Figure 7. The thermograms of the neat PVC and its low concentration nanocomposite (PVC-F10) have a similar plateau with a close thermal profile at the four zones mentioned before. However, the higher concentrations (PVC-F20, PVC-F30 and PVC-F40) show different and reformist profile by shifting the degradation temperatures to higher ones. It was reported that the nanostructures promoted the thermal stability of PVC [52]. Basically, the main areas of thermal decomposition correspond to the elimination of HCl “dehydrochlorination”, and the releasing of polyene radicals and unsubstituted aromatics [53]. In more details, Table 2 collects the thermal properties of degradation of PVC-green  $\text{CaCO}_3$  nanocomposite. F improved the thermal stability of the neat PVC as indicated by the sharp increase of  $T_{\text{onset}}$  from 208 °C to 221 °C, 243 °C, 260 °C and 274 °C respectively for PVC-F10, PVC-F20, PVC-F30 and PVC-F40. Furthermore; the higher  $T_{0.50}$  temperatures of nanocomposites affirm the thermal stability induced by the miscibility between PVC matrix and green F. The PVC-F30 and PVC-F40 have raised the  $T_{0.50}$  to 389 °C and 400 °C, compared with 358 °C for PVC as the most thermally stable nanocomposites. The taken filler has claimed the mass transport barrier against HCl degradation, and transfer the thermal degradation to higher temperatures indeed; related observations were reported elsewhere [54]. The residual ashes were increased dramatically corresponding to the more content of F nanofiller because of residue left from the nanocomposite; the higher percentage is more than 37%. This result suggests minimizing the evaporation rate of HCl during heating resulting in increasing of thermal properties. As a whole, the TGA results confirm the successful incorporation between PVC matrix and its fillers, which altered the thermal profile.

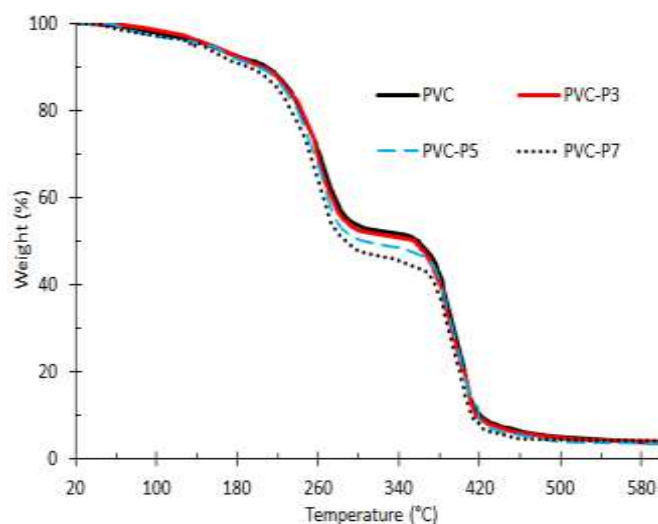
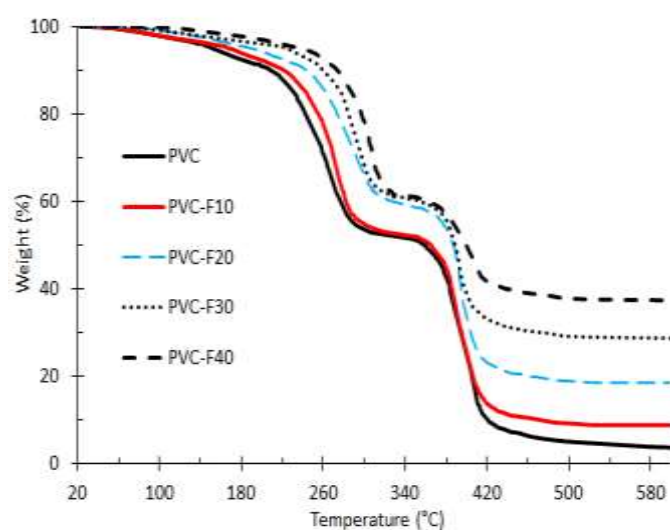


Figure 6: TGA of PVC-waste-based plasticizer composites.

Table 1: Fundamental results of thermal decomposition of PVC-waste-based plasticizer composite.

Sample	$T_{\text{onset}}$ (°C)	$T_{0.50}$ (°C)	R (%)
PVC	208	358	3.7
PVC-P3	204	355	3.9
PVC-P5	200	305	3.5
PVC-P7	191	288	4

Figure 7: TGA of PVC-green CaCO<sub>3</sub> nanocomposites.Table 2: Fundamental results of thermal decomposition of PVC-green CaCO<sub>3</sub> nanocomposite.

Sample	T <sub>onset</sub> (°C)	T <sub>0.50</sub> (°C)	R (%)
PVC	208	358	3.7
PVC-F10	221	366	8.8
PVC-F20	243	387	18.5
PVC-F30	260	389	28.7
PVC-F40	274	400	37.3

### 3.3. Migration test

The migration test investigates the resistance property of the plasticizer and filler to dislodge out of polymer matrix, in order to check the reliability for the application and to evaluate the efficiency of plasticization and processing. The migration of the prepared composites was performed using distilled water, ethanol anhydrous and petroleum ether environments. The specimens with dimensions of 20 x 20 mm<sup>2</sup> were soaked in 200 ml of the mentioned media for 24 h at room temperature. The soaked specimens were taken, wrapped off solvents on surface, dried overnight at 40 °C, and weighted again after exposure. The weight loss as the migration percentage was estimated according to Equation 1, where W<sub>0</sub> and W<sub>S</sub> donate the specimen weight before and after soaking in the different environments.

$$\text{Migration rate (\%)} = (W_0 - W_S) / W_0 \quad (1)$$

Figure 8(a) and (b) elucidate the percentages of migration rate of PVC-waste-based plasticizer composites, and PVC-green CaCO<sub>3</sub> nanocomposites in the different environments. Respectively, the distilled water, ethanol and petroleum ether simulate the aqueous, polar, non-polar environments. The composites show a good stability against migration; this is noticed within all environments due to the effective compatibility and good processing of the composites. The method of processing and the attachment between all constituents of composite strongly affect its physical characteristics in addition to mechanical properties [55]. The dual extrusion processing results in well-mixed PVC-fillers composites. It has a positive effect on stability against migration. Hence, the proposed waste-based plasticizer and green nanofiller can be beneficial to the lubrication among the segments of PVC matrix. The stability against migration in water and alcohol indicates the hydrophobic nature of composite. Furthermore, in the environment of petroleum ether, the composites show a higher rate of migration but still much lower than the limit. This agrees with some of findings that were declared elsewhere [56]. The indicated results confirm the physical stability and the positive effect of the fillers used, besides the effective extrusion processing technique, which minimizes the leaching rate.

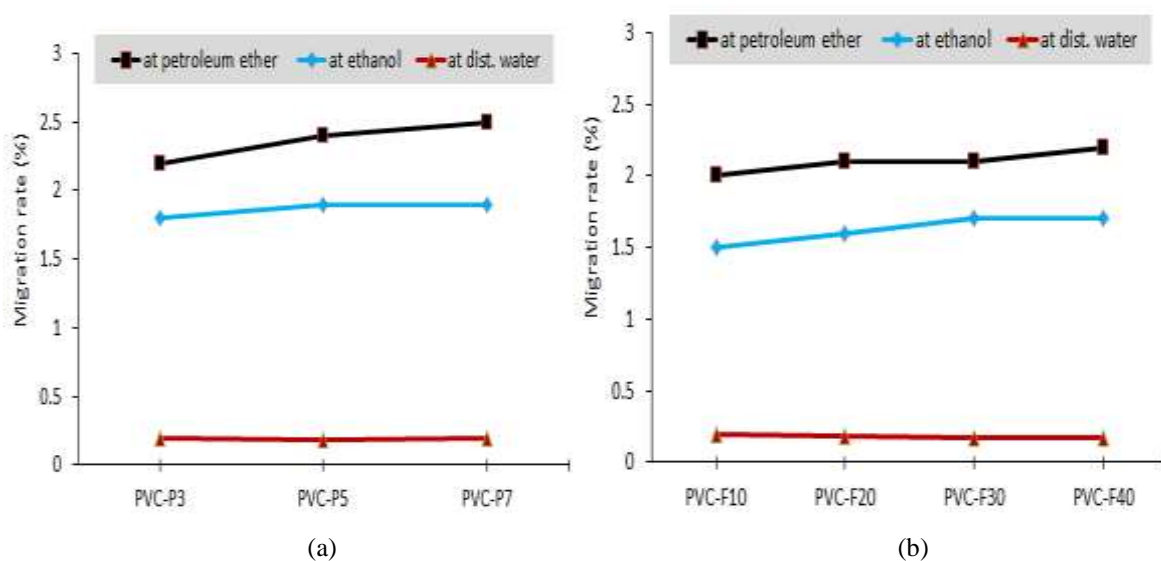


Figure 8: Migration test of PVC-waste-based plasticizer composites (a), and PVC-green CaCO<sub>3</sub> nanocomposites (b) in different media.

### 3.4. Hardness

The effect of adding P and F fillers on the surface mechanical property of PVC matrix was investigated by the Barcol impressor. In Figure 9, it is noticed that PVC-P3 and PVC-P5 have the same surface hardness at 48 BHC. They are a little bit lower than that of PVC at 49 BHC. However, the PVC-P7 composite decreased the surface hardness to 45 BHC. The plasticizers usually cause a reduction in some of mechanical properties of the matrix used, as a result of the smoothing and mellowing effect [57,58]. We can state that the highest concentration of our solid-waste plasticizer P lowers the surface stiffness of the recycled PVC matrix to a very little extent. However, the other concentrations i.e. PVC-P3 and PVC-P5 composites have acceptable hardness values. Regarding the effect of F on PVC matrix, the hardness was found to be increased with the more content of the green F nanoparticles. The impressor read 56 BHC, 61 BHC, 63 BHC and 62 BHC respectively for PVC-F10, PVC-F20, PVC-F30 and PVC-F40 nanocomposites, in comparison with the 49 BHC of neat PVC. As there is some drawback in PVC-F40, the addition concentration was stopped at this concentration of the proposed nanocomposite. The last observation is attributed to the accumulation phase of excess particles inside the polymer matrix, which negatively affect the nanocomposite product. It was described that the more concentrations of filler in different scales could deteriorate some of mechanical properties [59-61]. As per the obtained mechanical properties, the formula containing P5 and F30 can be considered as the optimized nanocomposite.

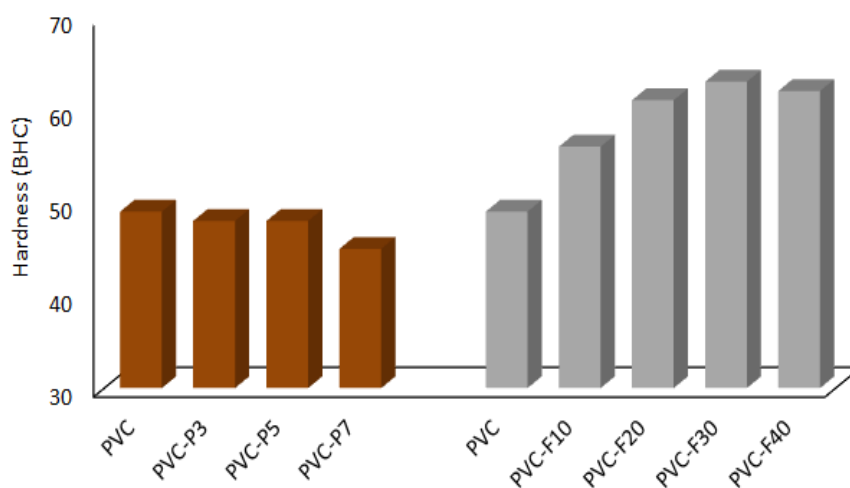


Figure 9: Hardness values of PVC-waste-based plasticizer composites, and PVC-green CaCO<sub>3</sub> nanocomposites.

### 3.5. Tensile properties

The tensile testing was done to the prepared composites for evaluating the mechanical properties after blending recycled PVC matrix with the proposed P plasticizer and green F nanofiller, as illustrated in Figure 10 and Figure 11, respectively. In more details, the achieved values of tensile strength, elongation, and elastic modulus are presented in Table 3 and 4 for the P- and F-based PVC. It is noticed that P resulted in decreasing the strength and increasing the strain, so the incorporated waste-based plasticizer supported the recycled PVC matrix with additional ductility. However, the incorporation of F nanofiller demonstrated a significant strength to PVC, and the elongation percentage was minimized with the more content of F. Specifically, the PVC-P3, PVC-P5 and PVC-P7 increased the elongation of PVC from 32% to 34%, 38% and 46%, respectively. The taken concentrations of P plasticizer increase the free volume among the segments of PVC. So the flexibility and sliding of the composite increase that leading to plasticization effect. The good plasticizers are able to enhance the elongation of the matrix [62]. However, these concentrations declined the value of tensile strength, especially with highest concentration (PVC-P7). In case of blending PVC with the prepared green F nanoparticles, the tensile strength respectively reached 20.5 MPa, 24.9 MPa, 31.9 MPa and 27 MPa for PVC-F10, PVC-F20, PVC-F30 and PVC-F40 nanocomposites, compared with the 19.4 MPa of blank PVC. The reason of the little decrease in the PVC-F40 specimen may be due to the aggregated structure upon excessive concentration, as noticed previously in the hardness section. The extra loading of nanofillers dramatically decreases the mechanical performance [63]. It is worth mentioning that the Young's modulus behaved in parallel with the tensile strength. Generally, the incorporation of P and F have different behaviors where the first improves the elasticity distinctly, and somewhat reduces the strength. Furthermore, the green F nanofiller maximizes the stress by more than 64%. The given data indicate the ability of prepared environmentally friendly plasticizer and nanofiller to improve the mechanical performance of the recycled PVC. The proposed additives are significantly applied in the recycled thermoplastics.

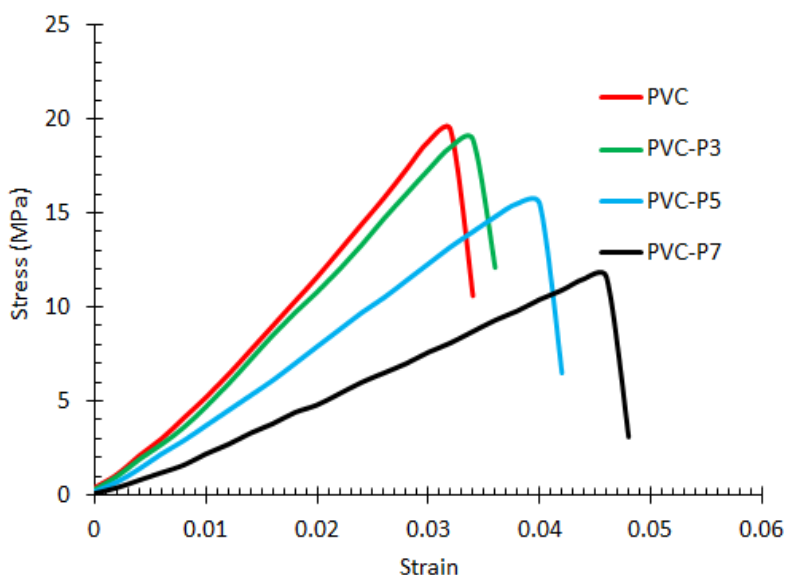
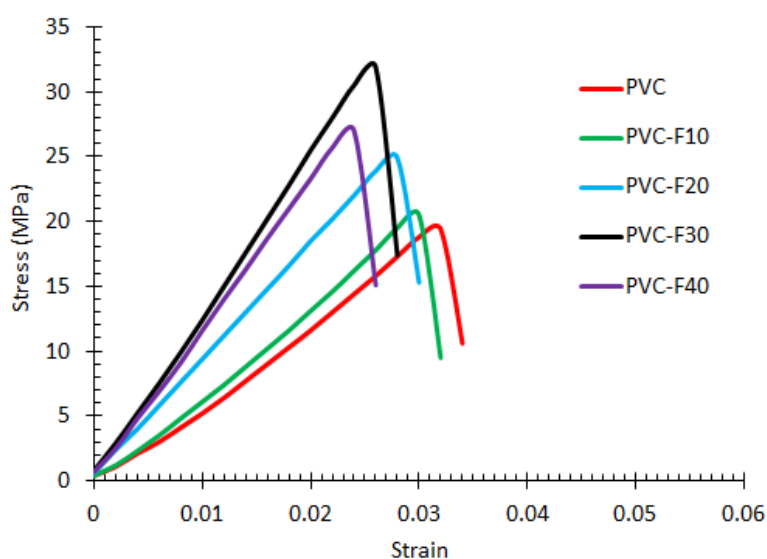


Figure 10: Tensile test of PVC-waste-based plasticizer composites.

Table 3: Details of tensile data for PVC-waste-based plasticizer composites.

Sample	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
PVC	19.4	32	643
PVC-P3	18.9	34	617
PVC-P5	15.5	38	419
PVC-P7	11.6	46	266



Figure 11: Tensile test of PVC-green  $\text{CaCO}_3$  nanocomposites.Table 4: Details of tensile data for PVC-green  $\text{CaCO}_3$  nanocomposites.

Sample	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
PVC	19.4	32	643
PVC-F10	20.5	30	700
PVC-F20	24.9	28	907
PVC-F30	31.9	26	1307
PVC-F40	27	24	1170

### 3.6. Application

The aim here is to apply the proposed composites as a water pipe. The prepared composites based on PVC-P5 and PVC-F30 were manufactured using the single extrusion of granulated particles. 12 m of 1 inch diameter pipe was formulated for this application. The proposed plasticized and filled composites showed enhanced applicable performance over the blank recycled PVC pipe. After analysis, the composites displayed neither damage nor leakage with applying 9 bar pressure. In contrast, the neat PVC pipe suffered from the water leakage. In a conclusion, the prepared waste-based plasticizer and green nanofiller-based PVC composites show improved properties, and can be employed in water pipe. This section approves the application as water pipe with the gained characteristics measured previously. Such enhanced character is being added to the environmentally friendly impact regarding the use of recycled PVC matrix, and the incorporated solid waste-based plasticizer and green nanofiller starting materials.

## 4. Conclusion

A new type of boosted and recycled polyvinyl chloride (PVC) was prepared. The modification was performed by plasticizing with a solid waste-based plasticizer and filling with a green  $\text{CaCO}_3$  nanofiller. The solid-waste waste plasticizer (P) was prepared by the glycolysis of polyethylene terephthalate waste (PET), and the source of nanofiller is the eggshells waste. Different concentrations of PVC-P and PVC-F composites were formulated via a single extrusion process, followed by hot pressing. The characterization sentence approves the successful obtaining of amorphous P plasticizer ester and crystalline F nanoparticles based on the microstructural testing. The thermal profile of the prepared composites was changed due to moving up the thermal degradation temperatures to higher degrees in the case of PVC-F nanocomposites. The plasticized PVC-P composites displayed little stability due to the effective plasticization. Furthermore, the proposed composites show improved physical and plasticizing properties regarding the lubrication of polymer segments. The composites show good stability against migration in different media due to their effective compatibility and good processing techniques. Mechanically, the addition of

more concentrations of P and F led to increased flexibility and strength, respectively. However, the values of surface hardness were promoted by the PVC-F composites by 30%. The data show the good plasticizing effect caused by the plasticizer P and the effective filling by the green F nanofillers. As per the obtained properties, the formula containing P5 and F30 can be considered the optimized nanocomposite. The proposed PVC-P5 and PVC-F30 were investigated as water pipes; they showed enhanced applicable performance over the blank recycled PVC pipe. The novelty aspect comes from the successful utilization of recycled PVC by environmentally friendly plasticizer and nanoparticles as enhanced water pipe composites. The proposed composites demonstrate a green advance over the virgin types. The added value PVC-P and PVC-F composites can share global trails for exploiting plastic and solid waste.

## 5. Conflicts of interest

There are no conflicts to declare.

## 6. References

- [1] Singh, N.; David, Hui; Singh, R.; Ahuja, I.P.S.; Feo, L.; Fraternali, F. Recycling of plastic solid waste: A state of art review and future Applications. *Compos. B. Eng.* **2017**, *115*, 409-422.
- [2] Cao, Q.; Yuan, G.; Yin, L.; Chen, D.; He, P.; Wang, H. Morphological characteristics of polyvinyl chloride (PVC) dechlorination during pyrolysis process: Influence of PVC content and heating rate. *Waste Manag.* **2016**, *58*, 241-249.
- [3] Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H.A. Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications. *Chem. Rev.* **2009**, *109*, 5437-5527.
- [4] Ahmad, N.; Mahmood, T. Preparation and properties of 4-aminobenzoic acid-modified polyvinyl chloride/titanium dioxide and PVC/TiO<sub>2</sub> based nanocomposites membranes. *Polym. Polym. Compos.* **2022**, *30*, 1-12.
- [5] Daniels, P.H. A brief overview of theories of PVC plasticization and methods used to evaluate PVC-plasticizer interaction. *J. Vinyl Addit. Technol.* **2009**, *15*, 219-223.
- [6] Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H. Thermal degradation of PVC: a review. *Waste Manag.* **2016**, *48*, 300-314.
- [7] Pearson, R.B. PVC as a food packaging material. *Food Chem.* **1982**, *8*, 85-96.
- [8] Braun, D. Poly (vinyl chloride) on the Way from the 19<sup>th</sup> Century to the 21<sup>st</sup> Century. *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 578-586.
- [9] Mohy Eldin, M.S.; Tamer, T.M.; Abu Saied, M.A.; Soliman, E.A.; Madi, N.K.; Ragab, I.; Fadel, I. Click grafting of chitosan onto PVC surfaces for biomedical applications. *Adv. Polym. Technol.* **2018**, *37*, 38-49.
- [10] Araújo, P.H.H.; Sayer, C.; Poco, J.G.R.; Giudici, R. Techniques for reducing residual monomer content in polymers: a review. *Polym. Eng. Sci.* **2002**, *42*, 1442-1468.
- [11] Bernard, L.; Décaudin, B.; Lecoeur, M.; Richard, D.; Bourdeaux, D.; Cuff, R.; Sautou, V. Analytical methods for the determination of DEHP plasticizer alternatives present in medical devices: a review. *Talanta* **2014**, *129*, 39-54.
- [12] Muszyński, M.; Nowicki, J.; Zygadlo, M.; Dudek, G. Comparison of Catalyst Effectiveness in Different Chemical Depolymerization Methods of Poly(ethylene terephthalate). *Molecules* **2023**, *28*, 6385.
- [13] Chanda M. Chemical aspects of polymer recycling. *Adv. Ind. Eng. Polym. Res.* **2021**, *4*, 133-150.
- [14] Abbas, M.I.; Sountharapandian, N.G.; Khudus, S.T. Surface bacterial adhesion study of novel ternary PVC/ polyester/ bentonite clay nanocomposite films. *Curr. Phys. Chem.* **2021**, *11*, 35-44.
- [15] Naguib, H.M. Environmental-friendly recycled Polyester/Mg(OH)<sub>2</sub> nanocomposite: Fire-retardancy and thermal stability. *Polym. Test.* **2018**, *72*, 308-314.
- [16] Hou, G.; Chen, J.; Lu, B.; Chen, S.; Cui, E.; Naguib, H.M. Guo, M.-Z.; Zhang, Q. Composition design and pilot study of an advanced energy-saving and low-carbon rankinite clinker. *Cem. Concr. Res.* **2020**, *127*, 105926.
- [17] Abo-Shanab, Z.L.; Ragab, A.A.; Naguib, H.M. Improved dynamic mechanical properties of sustainable bio-modified asphalt using agriculture waste. *Int. J. Pavement. Eng.* **2021**, *22*, 905-911.
- [18] Yin, B.; Aminlashgari, N.; Yang, X.; Hakkarainen, M. Glucose esters as biobased PVC plasticizers. *Eur. Polym. J.* **2014**, *58*, 34-40.
- [19] Mohamed, M.R.; Naguib, H.M.; El-Ghazawy, R.A.; Shaker, N.O.; Amer, A.A.; Soliman, A.M.; Kandil, U.F. Surface activation of wood plastic composites (WPC) for enhanced adhesion with epoxy coating. *Mater. Perform. Charact.* **2019**, *8*, 22-40.
- [20] Xu, Z.; Yu, L.; Lu, B.; Sun, J.; Liu, Z.; Naguib, H.M.; Hou, G. Aragonite formation induced by triethylene glycol and its enhancement to flexural strength in carbonated rankinite cement. *Constr. Build. Mater.* **2023**, *408*, 133514.
- [21] Naguib, H.M.; Hou, G.; Chen, S.; Yao, H.; Lu, B.; Chen, J. Mechanisms and Optimal Reaction Parameters of Accelerated Carbonization of Calcium Silicate. *Kuei Suan Jen Hsueh Pao/ J. Chin. Ceram. Soc.* **2019**, *47*, 1175-1180.
- [22] Hou, G.; Yan, Z.; Sun, J.; Naguib, H.M.; Lu, B.; Zhang, Z. Microstructure and mechanical properties of CO<sub>2</sub>-cured steel slag brick in pilot-scale. *Constr. Build. Mater.* **2021**, *271*, 121581.
- [23] Feng, S.; Zhang, P.; Jiang, P.; Zhang, Z.; Deng, J.; Cao, Z. Synthesis and application of high-stability bio-based plasticizer derived from ricinoleic acid. *Eur. Polym. J.* **2022**, *169*, 111125.
- [24] Atta, M.M.; Henaish, A.M.A.; Elbasiony, A.M.; Taha, E.O.; Dorgham, A.M. Structural, optical, and thermal properties of PEO/PVP blend reinforced biochar. *Opt. Mater.* **2022**, *127*, 112268.
- [25] Atta, M.M.; Taha, E.O.; Abdelreheem, A.M. Nitrogen plasma effect on the structural, thermal, and dynamic mechanical properties of PVA/starch/graphene oxide nanocomposite. *Appl. Phys. A* **2021**, *127*, 532.

- [26] Calosi, M.; Renon, M.; Belletti, G.; Mazzanti, V.; Mollica, F.; Massi, A.; Bertoldo, M. Glycolysis of semi-interpenetrated polymer network foam based on poly(vinyl chloride) for recovery and reuse of the individual components. *Waste Manag.* **2022**, *153*, 229-239.
- [27] Amaro, L.P.; Coiai, S.; Ciardelli, F.; Passaglia, E. Preparation and testing of a solid secondary plasticizer for PVC produced by chemical degradation of post-consumer PET. *Waste Manag.* **2015**, *46*, 68-75.
- [28] Ali, M.; Lu, Y.; Ahmed, S.; Khanal, S.; Xu, S. Effect of modified cardanol as secondary plasticizer on thermal and mechanical properties of soft polyvinyl chloride. *ACS Omega* **2020**, *5*, 17111-17117.
- [29] Naguib, H.M.; Hou, G. Vinylyster-glass fiber composite for water pipe: Processing and effect of fiber direction. *Egypt. J. Pet.* **2023**, *32*, 24-30.
- [30] Alnajjar, H.M.; Naguib, H.M.; Shaker, N.O.; Ahmed, H.; Farag, A.A.; Kandil, U.F. Enhancement of recycled WPC with epoxy nanocomposite coats. *Egypt. J. Chem.* **2019**, *62*, 555–563.
- [31] Lin, Z.Z.; Wang, Y.; Yang, X.-B.; Yan, S.-R.; Chen, Y.; Li, H.-C.; Wang, G. Strengthening soft poly(vinyl chloride) plastics via three-arm star copolymeric plasticizers. *Mater. Today Commun.* **2023**, *35*, 105847.
- [32] Gao, W.; Jiang, P.; Gu, Q.; Zhang, H.; Zhang, P.; Haryono, A. Synthesis and properties of a bio-based PVC plasticizer derived from lactic acid. *New J. Chem.* **2021**, *45*, 123-130.
- [33] Yin, X.; Zhang, J.; Zhang, Z.; Xu, G. Tailoring the desired optical and mechanical performance of polyester-plasticized PVC films: the role of different light stabilizers on the photo-degradation. *Polym. Adv. Technol.* **2017**, *28*, 1831–1841.
- [34] Jia, P.; Hu, L.; Feng, G.; Bo, C.; Zhang, M.; Zhou, Y. PVC materials without migration obtained by chemical modification of azide-functionalized PVC and triethyl citrate plasticizer. *Mater. Chem. Phys.* **2017**, *190*, 25-30.
- [35] Yuan, J.; Cheng, B. A Strategy for Nonmigrating Highly Plasticized PVC. *Sci. Rep.* **2017**, *7*, 9277.
- [36] Yu, Q.; Selvadurai, A.P.S. Mechanical behaviour of a plasticized PVC subjected to ethanol exposure. *Polym. Degrad. Stab.* **2005**, *89*, 109-124.
- [37] Greco, A.; Ferrari, F.; Maffezzoli, A. UV and thermal stability of soft PVC plasticized with cardanol derivatives. *J. Clean. Prod.* **2017**, *164*, 757-764.
- [38] Elicegui, A.; del Val, J.J.; Bellenger, V.; Verdu, J. A study of plasticization effects in poly (vinyl chloride). *Polym.* **1997**, *83*, 1647-1657.
- [39] Tsumura, Y.; Ishimitsu, S.; Kaihara, A.; Yoshii, K.; Nakamura, Y.; Tonogai, Y. Di(2-ethylhexyl) phthalate contamination of retail packed lunches caused by PVC gloves used in the preparation of foods. *Food Addit. Contam.* **2001**, *18*, 569-579.
- [40] Kim, J.H.; Kim, S.H.; Lee, C.H.; Nah, J.W.; Hahn, A. DEHP migration behavior from excessively plasticized PVC sheets. *Bull. Korean Chem. Soc.* **2003**, *24*, 345-349.
- [41] Naguib, H.M. Recycled polyester filled with eggshells waste-based nano CaCO<sub>3</sub>; thermo-mechanical and flame-retardant features. *New J. Chem.* **2023**, *47*, 4999–5010.
- [42] Atta, A.M.; Elnagdy, S.I.; Abdel-Raouf, M.E.; Elsaeed, S.M.; Abdel-Azim, A.A. Compressive properties and curing behaviour of unsaturated polyester resins in the presence of vinyl ester resins derived from recycled poly (ethylene terephthalate). *J. Polym. Res.* **2005**, *12*, 373-383.
- [43] Naguib, H.M.; Hou, G. Exploitation of Natural and Recycled Biomass Resources to Get Eco-friendly Polymer. *J. Polym. Environ.* **2023**, *31*, 533–540.
- [44] Vagenas, N.; Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy. *Talanta* **2003**, *59*, 831–836.
- [45] Spanos, N.; Koutsoukos, P.G. The transformation of vaterite to calcite: effect of the conditions of the solutions in contact with the mineral phase. *J. Cryst. Growth* **1998**, *191*, 783–790.
- [46] Bal, S.; Behera, R.C. Structural Investigation of Chemical Treated Polyester Fibers Using Saxs and Other Techniques. *J. Miner. Mater. Charact. Eng.* **2006**, *5*, 179-198.
- [47] Naguib, H.M.; Zhang, X.H. Advanced recycled polyester based on PET and oleic acid. *Polym. Test.* **2018**, *69*, 450–455.
- [48] Cosentino, I.; Liendo, F.; Arduino, M.; Restuccia, L.; Bensaid, S.; Deorsola, F.; Ferro, G.A. Nano CaCO<sub>3</sub> particles in cement mortars towards developing a circular economy in the cement industry. *Procedia Struct. Integr.* **2020**, *26*, 155-165.
- [49] Deffo, G.; Basumatary, M.; Hussain, N.; Hazarika, R.; Kalita, S.; Njanja, E.; Puzari, P. Eggshell nano-CaCO<sub>3</sub> decorated PANi/rGO composite for sensitive determination of ascorbic acid, dopamine, and uric acid in human blood serum and urine. *Mater. Today Commun.* **2022**, *33*, 104357.
- [50] Abaci, U.; Guney, H.Y.; Yilmazoglu, M. Plasticizer effect on dielectric properties of poly(methyl methacrylate)/titanium dioxide composites. *Polym. Polym. Compos.* **2021**, *29*, S565-S574.
- [51] Jia, P.; Hu, L.; Shang, Q.; Wang, Q.; Zhang, M.; Zhou, Y. Self-plasticization of PVC materials via chemical modification of mannich base of cardanol butyl ether. *ACS Sustain. Chem. Eng.* **2017**, *5*, 6665-6673.
- [52] Ahmed, R.M.; Atta, M.M.; Taha, E.O. Optical spectroscopy, thermal analysis, and dynamic mechanical properties of graphene nano-platelets reinforced polyvinylchloride. *J. Mater. Sci.: Mater. Electron.* **2021**, *32*, 22699–22717.
- [53] Wang, Y.-K.; Tsai, F.-C.; Ma, C.-C.; Wang, M.-L.; Kuo, S.-W. Using methacryl-polyhedral oligomeric silsesquioxane as the thermal stabilizer and plasticizer in poly(vinyl chloride) nanocomposites. *Polym.* **2019**, *11*, 1711.
- [54] Fathy, E.S.; Elnaggar, M.Y.; Hassan, M.M. Thermo-mechanical properties of polyvinyl chloride/vulcanized nitrile butadiene rubber blends cured by gamma irradiation. *Egypt. J. Radiat. Sci. Appl.* **2018**, *31*, 1-11.
- [55] Awad, E.H.; El-Nemr, K.F.; Atta, M.M.; Abdel-Hakim, A.; Sharaf, A. Electromagnetic interference shielding efficiency of irradiated wood-plastic composites based on graphene oxide nanoparticles. *Radiat. Phys. Chem.* **2023**, *203*, 110629.

- 
- [56] da Silva, M.A.; Vieira, M.G.A.; Maçumoto, A.C.G., Beppu, M.M. Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid. *Polym. Test.* **2011**, *30*, 478-484.
- [57] Tarique, J.; Sapuan, S.M.; Khalina, A. Effect of glycerol plasticizer loading on the physical, mechanical, thermal, and barrier properties of arrowroot (*Maranta arundinacea*) starch biopolymers. *Sci. Rep.* **2021**, *11*, 13900.
- [58] Bakar, M.; Djaidar, F. Effect of plasticizers content on the mechanical properties of unsaturated polyester resin. *J. Thermoplast. Compos. Mater.* **2007**, *20*, 53-64.
- [59] Younus, M.M.; Naguib, H.M.; Fekry, M.; Elsayy, M.A. Pushing the limits of PLA by exploring the power of MWCNTs in enhancing thermal, mechanical properties, and weathering resistance. *Sci Rep.* **2023**, *13*, 16588.
- [60] Naguib, H.M.; Ahmed, M.A.; Abo-Shanab, Z.L. Studying the loading impact of silane grafted Fe<sub>2</sub>O<sub>3</sub> nanoparticles on mechanical characteristics of epoxy matrix. *Egypt. J. Pet.* **2019**, *28*, 27-34.
- [61] Zhang, Y.; Ding, C.; Zhang, N.; Wang, Y.; Zhang, Y.; Li, H.; Zhang, Y. Formulation optimization and performance enhancement of polyvinyl chloride-silica micropowder composites with a promising flooring application. *J. Mater. Res. Technol.* **2023**, *26*, 8944-8960.
- [62] Ledniowska, K.; Nosal-Kovalenko, H.; Janik, W.; Krasuska, A.; Stańczyk, D.; Sabura, E.; Bartoszewicz, M.; Rybak, A. Effective, environmentally friendly PVC plasticizers based on succinic acid. *Polym.* **2022**, *14*, 1295.
- [63] Naguib, H.M.; Taha, E.O.; El-Deeb, A.S.; Abdel Kader, M.M.; Ahmed, M.A. Influence of chromium oxide nanoparticles and fiber fillers on silicone rubber nanocomposite. *Polym. Bull.* **2024**, *81*, 9795-9812.