Wooden Polymer Composites of Poly(vinyl chloride), Olive Pits Flour, and Precipitated Bio-Calcium Carbonate

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ABSTRACT: As a filler to be inserted into poly(vinyl chloride) (PVC), low-cost olive pits flour (OPF) and precipitated bio-calcium carbonate (PBCC)-produced PVC/OPF/PBCC composites have been used with high stability and rigidity compared to PVC. Hydrogen bonding is generated between OH cellulose in OPF and H in PVC. Composite tensile modulus increased in PVC grid in the presence of PBCC and OPF, possibly because of a filler restriction effect on the polymer chains. The hardness also increased as both OPF and PBCC increased. The mechanical tendency of the PVC/OPF composite was improved by adding a low content of PBCC particles with the PVC network, resulting in a smart distribution in the range of 10% by weight, and it was reduced by adding more than that percentage. The successful distribution of PBCC in PVC/OPF composite strengthened the mechanical path. The morphology and possible interface adhesion of components in the composite were demonstrated by scanning electron microscopy (SEM). The PVC SEM images showed a homogeneous, smart, and consistent surface, while the PVC/60 wt % OPF SEM images showed a large number of voids that suggested weak PVC/OPF interactions. The SEM images showed outstanding PBCC distribution in the PVC/OPF matrix for the PVC/50 wt % OPF/10 wt % PBCC composite. Due to the accumulation of PBCC particles producing cavities, the distribution of particles became nonhomogeneous at percentages above 10 wt %. At a low filler material, better spread of PBCC particles in the PVC grid was achieved. Owing to the polarity of OPF, the H2O absorption and thickness swelling of PVC/OPF/PBCC composites showed higher amounts than PVC. PBCC improved the thermal stabilization and the neutralization of Cl− negative ions as an acid acceptor of secondary PVC stabilization.

1. INTRODUCTION

Polymers are used in day-to-day life, namely, rubber, plastic, and resins and are labeled in accordance to their origin, such as natural rubber and silk, starch, semisynthetic modified polymers, cellulosic compounds, and synthetic ones (polyolefins, polyesters, polyethers, and PVC).1−3 PVC is used in pipes, electric powered wires, window profiles, etc. It has proper mechanical properties, fire and fungus opposing and lengthy lifetime.5−8 PVC produced by cracking from petroleum or natural gas bears a randomly disbursed molecular weight with a degree of viscosity with some additives that govern its physical, thermal, and mechanical characters and improve cost, processability, durability, weather resistance, color, and electrical performance.9−11 Heat stabilizers like tribasic PbSO4 and lead compounds increase thermal degradation concerning PVC, discoloration, and decay of both mechanical and chemical properties. Processing aids like methyl methacrylate (MMA) encourage the melt flow during manufacturing and improve the transparent look. Impact modifiers like chlorinated polyethylene (CPE) or acrylonitrile-butadiene-styrene terpolymer (ABS) rubbery copolymers are matching with PVC to increase impact strength and achieve ductility weathering.12,13 Some additives act as lubricants to reduce the frictional resistance inside polymer matrix.14 Antioxidants and stabilizers are free radicals’ scavengers or phenol derivatives that can stop peroxide radicals from degrading hydroperoxide, change inactive derivatives via chemical reaction, and enhance both thermal and optical properties of PVC. Hydroxy-benzophenone and hydroxyl-phenyl triazole are considered as light stabilizers dissipating UV diffraction prior to degradation that prevent permanent chemical change.15 Fillers exchange a part of plastic yet decrease cost, improve properties yet performance such as CaCO3 filler in calcite mineral could be able to keep as grounded to a particular particle size.11 Coated CaCO3 with stearic acid, as a common cover of CaCO3 that minimize longevity attention of wetness during storage and bulk agglomeration during the mixing

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process, reduces interfacial tension, H₂O absorption, adsorption on processing aids, and impingement of polymer melt and then enhance melt flowing features. Coated CaCO₃ with a common particle dimension of 1 µm has a positive effect on the impact strength of PVC to be used for window line production and many applications. Fillers components have unique properties different from PVC relying on every component properties and the interface factors between components over last made-up production. Natural fibers were used in high percentages in commercial WPC products to enhance durability, mechanical strength performance, interfacial quality of WPCs, the manufacturing rate, and reduces the rate of H₂O absorption. Studies on PVC performance with some fibers and coupling agents are available. Reinforcing materials, olive waste has rising potential among many other applications. Cornwell showed that calcium carbonate increases the impact strength of PVC and proved it especially for PBCC in PVC. This work aims at evaluating the effect of waste fiber (OPF) and PBCC on the physical, mechanical, thermal, and morphological properties of PVC to produce new costless WPCs and manage wastes that pollute the environment. Characterization of PVC/OPF/PBCC composites using SEM, FTIR, TGA, and DSC, as well as mechanical characters, water uptake, thickness swelling, and specific gravity measurements were done.

2. EXPERIMENTAL SECTION

2.1. Materials. PVC powder (K-value = 67, d: 5 × 10⁻² to 56 × 10⁻² g/mL, inherent viscosity = 92 × 10⁻²) was provided by Egyptian Petrochemical Co. Chlorinated polyethylene (CPE) was introduced in PVC/OPF/PBCC composites as a toughening modifier to compatibilize polymer lattice with the filler enhancing melt process. Tribasic lead sulfate (TBLS), dibasic lead stearate (DLST), and lead stearate (NLST) have been utilized as thermal stabilizers; stearic acid, polyethylene wax, and calcium stearate (CaSt) have been utilized as lubricants; titanium dioxide (TiO₂) has been used as a photoactive agent; and acrylic processing resource (K-120) has been used to facilitate processing. All compounds were photoactive agent; and acrylic processing resource (K-120) has been used to facilitate processing. Cornwell showed that calcium carbonate increases the impact strength of PVC and proved it especially for PBCC in PVC. This work aims at evaluating the effect of waste fiber (OPF) and PBCC on the physical, mechanical, thermal, and morphological properties of PVC to produce new costless WPCs and manage wastes that pollute the environment. Characterization of PVC/OPF/PBCC composites using SEM, FTIR, TGA, and DSC, as well as mechanical characters, water uptake, thickness swelling, and specific gravity measurements were done.

3. RESULTS AND DISCUSSION

3.1. PBCC Analysis. CaCO₃ material content in PBCC was measured using volumetric techniques. It gives 81.6 at 9.38% moisture content (ASTM D3030), a density of 0.745 g/mL (ASTM D1895), and a dioctyl phthalate, (DOP) uptake of 54/100 g (ASTM D3367). Evaluation was made at Polymer Lab at Scientific Research, Alexandria.13 Specified gravity was calculated as

\[ \text{Sp. gr.} = \frac{a}{(a + b - m)} \]

where \( a \) is the sample weight, \( b \) is the weight of pycnometer filled with H₂O, and \( m \) is the weight of pycnometer with sample.

Thermogravimetric analysis (TGA) in accordance with ASTM D 3850-94-ASTM 2012 using a PerkinElmer device (TGA-50H) was performed between 25 and 500 °C with N₂ (g) surroundings at a rate of 10 °C/min in a Pt cell at the City of Scientific Research, Egypt. Differential scanning calorimetry (DSC) was performed in accordance with ASTM D 3418-03-ASTM 2012 in DSC, 60-A SHIMADZU. Each composite (5–10 mg) was positioned in Al capsules and then heated in the range of 25–250 °C under N₂ (g) flow at a rate of 5 °C min⁻¹ at Polymer Lab, City of Scientific Research, Alexandria.13 Laser diffraction measurement of PBCC particles distribution was performed using a Beckman Coulter instrument with an M5-Submicron analyzer at City of Scientific Researches, Alexandria. Two particle size averages were obtained at two angles matching of rod and sphere with dimensions of (875–196) × 10⁻³ and (840–270) × 10⁻³ µm (rod-shaped particles) and (30–82) × 10⁻³ µm (spherical-shaped particles) as shown in Figure 1. Different shapes may be generated under the effect of CO₂ injection rate and temperature during PBCC extraction. Laser diffraction measurement of PBCC particles distribution was done using a Beckman Coulter instrument with an M5-Submicron analyzer at City of Scientific Researches, Alexandria. Two particle size averages were obtained at two angles matching for the two shapes of PBCC particles, 351 nm at 11.1° and 898.5 nm at 90°, as explained in Figure 2. An EDX detector (JEOL-JSM 6360LA) together with advanced vacuum technique was used to detect different elements and oxides in PBCC. Results are recorded in Figure 3 and explained in Tables 1 and 2. Two roll mill compression molding was utilized to prepare the proposed compositions. PVC compound without OPF and PBCC were mixed along with components in a TRL-20 C turbo mixer (5 L) at 2000 rpm and 115 °C, then cooled at 40 °C, cast to PE sacks, loaded with OPF and PBCC, and finally introduced to Betol Machinery Ltd., UK, at 180 °C to obtain PVC/OPF/PBCC sheets with different compositions as listed in Tables 3 and 4. Optical performance of PBCC was evaluated in accordance with ASTM standard D 3850-94-ASTM 2012 using a PerkinElmer device (TGA-50H) was performed between 25 and 500 °C with N₂ (g) surroundings at a rate of 10 °C/min in a Pt cell at the City of Scientific Research, Egypt.
μm that dried at 105 ± 3 °C for 48 h to eliminate moisture as much as possible until reaching fixed weight in accordance with ASTM D-1037 at the Faculty of Agriculture, Alexandria University.

### 3.3. FTIR Spectra

Figure 4 shows the different functional groups of PVC, PBCC, and OPF, as well as the interactions of components in such compositions. PVC illustrates peaks at 616 cm⁻¹ for C–Cl stretching vibration, 970 cm⁻¹ for rocking CH₂, 1095 cm⁻¹ for (C–C) stretching vibration, 1250 cm⁻¹ for C–H stretching from CH–Cl, 1330 cm⁻¹ for CH₂ deformation, 1430 cm⁻¹ for wagging CH₂ group, 1745 cm⁻¹ for (C=O) stretching vibration, 1640 cm⁻¹ for (C=C) stretching vibration, 1510 cm⁻¹ for (C=C) aromatic skeletal vibrations, and 1405 cm⁻¹ for (C=O) stretching vibration owing to the wagging (CH₂) group. The presence of PBCC in PVC composites was demonstrated by a new peak assignment at 873 cm⁻¹ that was caused by (C=O) stretching vibration. Also, the peak of OPF around 3350 cm⁻¹ for (O=H) stretching was shifted to a lower frequency (3410 cm⁻¹) upon adding to PVC. This is might be because of H bonds produced among –OH groups of cellulose/lignin in OPF and α-H in PVC, confirming an interaction between OPF and PVC.

### 3.4. Morphological Characteristics

SEM results confirmed the morphology micrographs and interfacial interference of OPF and PBCC within PVC chains. Figures 5 and 6 show the

![Figure 1. PBCC morphology with (a) 15 000x and (b) 20 000x magnification.](image1)

![Figure 2. PBCC particle size distribution.](image2)

![Figure 3. Analysis of PBCC elements.](image3)

![Table 1. Elements Analysis of PBCC by EDX](table1)

| element     | wt % | element     | wt % |
|-------------|------|-------------|------|
| carbon      | 11.15| chromium    | 0.06 |
| oxygen      | 32.81| manganese   | 0.31 |
| sodium      | 0.20 | iron        | 0.43 |
| magnesium   | 1.48 | cobalt      | 0.32 |
| aluminum    | 0.48 | nickel      | 0.01 |
| silicon     | 0.86 | copper      | 0.45 |
| phosphorus  | 0.74 | zinc        | 0.38 |
| sulfur      | 0.42 | strontium   | 0.39 |
| potassium   | 0.21 | cadmium     | 0.08 |
| calcium     | 49.13| lead        | 0.33 |

OPF gave a band around 3350 cm⁻¹ for cellulosic (O=H) stretching, 2925 cm⁻¹ for (C=H) symmetrical stretching vibration, 1745 cm⁻¹ for (C=O) stretching, 1640 cm⁻¹ for (C=C) stretching vibration, 1510 cm⁻¹ for (C=C) aromatic skeletal vibrations, and 1405 cm⁻¹ for (C=O) stretching vibration owing to the wagging (CH₂) group. As appeared in A2, AS spectra, the PVC peak at 1430 cm⁻¹ was overlapped by the PBCC, indicative peak of intensity at 1426, 1427 cm⁻¹ of (C–H) bending vibration owing to the wagging (CH₂) group. The presence of PBCC in PVC composites was demonstrated by a new peak assignment at 873 cm⁻¹ that was caused by (C=O) bending vibration. Also, the peak of OPF around 3350 cm⁻¹ for (O=H) stretching was shifted to a lower frequency (3410 cm⁻¹) upon adding to PVC. This is might be because of H bonds produced among –OH groups of cellulose/lignin in OPF and α-H in PVC, confirming an interaction between OPF and PVC.
Composites generate severe problems because of the agglomeration of loadings increased in A3 and A4 samples, the distribution of the interfacial adhesion of the components. When PBCC PVC/OPF regarding A2 sample of 10 wt % PBCC and enhanced a superior distribution occurred at paltry PBCC content in resulting in bad stress transfer through the polymer and the poor interaction of OPF along the PVC grid. Some of the OPF samples. PVC showed the homogeneous and uniform surface. SEM micrographs of the fractured surfaces of PVC/OPF/PBCC.

Table 2. Oxides Analysis in PBCC by EDX

| oxides          | wt %  |
|-----------------|-------|
| sodium oxide    | 0.43  |
| magnesium oxide | 2.68  |
| aluminum oxide  | 0.97  |
| silicon oxide   | 2.01  |
| phosphorus oxide| 1.24  |
| sulfur oxide    | 1.17  |
| potassium oxide | 0.29  |
| chromium oxide  | 0.09  |
| manganese oxide | 0.45  |
| ferrous oxide   | 0.61  |
| cobalt oxide    | 0.3   |
| nickel oxide    | 0.01  |
| copper oxide    | 0.63  |
| zinc oxide      | 0.33  |
| strontium oxide | 0.5   |
| cadmium oxide   | 0.1   |
| lead oxide      | 0.68  |

Table 3. PVC Components (PVC Compound)

| type              | Phr. |
|-------------------|------|
| PVC               | 100  |
| CPE               | 2    |
| TBL5              | 3    |
| DRLST             | 1    |
| NLST              | 0.5  |
| K120              | 1.5  |
| Ca-stearate       | 0.5  |
| stearic acid      | 1    |
| polyethylene wax  | 1    |
| TiO2              | 1    |

Table 4. Compositions of Different PVC/OPF/PBCC Composites

| samples | PVC | OPF | PBCC |
|---------|-----|-----|------|
| A0      | 100 | 60  |      |
| A1      | 40  | 60  | 10   |
| A2      | 40  | 50  | 20   |
| A3      | 40  | 50  | 30   |
| A4      | 40  | 30  | 30   |
| A5      | 40  | 60  | 30   |

Table 5. OPF Components Analysis

| fiber | lignin (wt %) | cellulose (wt %) | hemicelluloses (wt %) | ash content (%) | average bulk density (g/mL) |
|-------|---------------|------------------|-----------------------|-----------------|-----------------------------|
| OPF   | 33.67         | 48.62            | 16.78                 | 0.93            | 0.21                        |

PBCC particles related to its small size and high polar property. At greater percentages of PBCC in A5, the aggregated particles have a negative effect on the adhesion of PBCC along PVC, producing agglomeration sites and cavities inside the polymer matrix.13,40

3.5. Mechanical Outcomes. Tensile strength, tensile modulus, and strain at break of all composites are given in Table 6. Stress−strain curve confirmed the toughening behavior; strain at break, and tensile strength of PVC/OPF/PBCC compositions. The tensile strength of PVC is 41.76 MPa, giving ductile failure. On adding OPF, the failure mode immediately shifts from ductile to brittle, which is much stiffer. The tensile strengths of A1, A2, A3, A4, and A5 samples were 22.78, 29.21, 24.14, 21.06, and 20.85 MPa, respectively. This decrease compared to PVC may be due to the limitations imposed by OPF and PBCC molecular movements and poor interaction of OPF with PVC chains.41,42 Fine and regular particles of PBCC improved the mechanical properties of PVC.33 The tensile strengths of the A2 composite at 10 wt % PBCC and 50 wt % OPF are higher than that of A1, which has 60 wt % OPF; this may be due to the good distribution of PBCC particles in PVC and interfacial binding between polymer and filler, facilitating transfer of stress to the filler. Higher PBCC loadings lead to particle agglomeration and thus larger observed particles, which affect the toughness of the resultant composites and decrease the tensile strength of the A2, A3, and A4 samples. The tensile strength of A5 specimen indicating a better dispersion of PBCC than OPF particles in PVC. The olive pits flour induces swelling within the matrix, generating an important pressure deteriorating the mechanical properties. The tensile modulus of high OPF and/or PBCC loadings increased from 1164 MPa for PVC to 1455 for A1 and 2198 for A2, and then decreased to 1837 for A3, 1689 for A4, and 1617 MPa for A5. The increase of tensile modulus may be due to the restraining action of the fillers on PVC lattice. The A2 sample has the highest tensile modulus because PBCC particles strongly affect elastic modulus when incorporated in low contents, which results in a homogeneous dispersion of PBCC and less agglomeration in the PVC matrix. Tensile modulus decreased significantly from 2198 MPa for A2 to 1837, 1689, and 1617 MPa for A3, A4, and A5 composites, respectively. Dispersion becomes a severe problem that can be described as particles with higher dimension and smaller surface contact area that lead to development of cavities and interface debonding that affect the mechanical behavior of the polymer. The strain at break changed from 87.42% for PVC to 2.97% for A1, 3.11% for A2, 3.20% for A3, 3.36% for A4, and 3.65% for A5. This may be due to the effect of OPF and PBCC on the polymer chain mobility and the deformability of a rigid interface created between OPF/PBCC and PVC.13,44

Table 7 indicates that the principal values of notched strength of the Izod impact on composites PVC/OPF/PBCC are significantly reduced by the presence of OPF that diminishes PVC ductility and gives more frictional effects.45 The impact strength of A2 is greater than those of A1, A3, A4, and A5 due to the finer PBCC dispersion in the PVC matrix. There were still some agglomerations at higher PBCC load levels, which led to larger observed particle size and gradually decreased impact strength.46 With the inclusion of OPF in the matrix, the impact of PVC significantly decreases, progressively improves with the addition of 10 wt % PBCC, then decreases again significantly with the increase in PBCC content due to its agglomeration, and...
affects the interfacial compatibility that allows the impact strength to be reduced.\textsuperscript{13}

Table 8 indicates a decrease in flexural strength to 44.74 MPa for A1 due to a weak dispersion of fiber and a failure to adhere interfacially. Because of the fine distribution of PBCC particles into the matrix, the flexural strength of A2 is greater than those of A1, A3, A4, and A5. The A5 composite that includes 60 wt % PBCC gives a considerably higher value compared to A1 due to the absence of OPF.

Composites’ hardness with OPF and PBCC applied greatly increases as shown in Table 9. Hardness increases considerably from 76 for A0 to 86 for A5 that may be clarified by the rigid characteristics of PBCC and OPF.

3.6. Water Absorption. \(\text{H}_2\text{O}\) absorption data of various components are obtained at various immersion times 2, 24, 168, 336, 672, and 1008 h. Hydrogen bonding sites are responsible for such results.\textsuperscript{47} Table 10 represents that the absorption of \(\text{H}_2\text{O}\) of the A0 sample reached 0.38\% after 1008 h of immersion, while the absorption for A1 was 15.68\%, A2 was 12.28\%, A3 was 9.24\%, and A4 was 8.9\%, and A5 was 0.75\%. \(\text{H}_2\text{O}\) absorption in composites depends on the OPF loads. The \(\text{H}_2\text{O}\) absorption of composites is affected by high wt % of OPF. OPF comprises many free groups of hydroxyl (\(\text{O}−\text{H}\)) usable for contact water via hydrogen bonding. With increased OPF loading, water absorption in the composite systems increased drastically for three reasons: hydrogen bonding of \(\text{H}_2\text{O}\) molecules with \(\text{OH}\) in
OPF, water molecule diffusion into the filler–matrix interfaces, and the broad variety of tubular pores in the fiber. The H$_2$O absorption of A1 composite was increased to 15.68% after 1008 h. In A2, voids and cavities decreased due to PBCC fine distribution, which improved the interface adhesion between filler and PVC matrix preventing the increase of absorbed H$_2$O.

Composite thickness swelling is similar to H$_2$O absorption. Composites showed high thickness swelling as shown in Figure 7. As cellulose is the principal component in OPF, absorbed H$_2$O is mainly located on a wooden fiber/polymer matrix interface. The thickness swelling of A0 increases from 0.31% after 2 h to 0.61% after 24 h and reached a constant value of 0.92% after 168 h until 1008 h because of the hydrophobic aspect of PVC. H$_2$O absorption increment is due to the compatibility of hydrophilic OPF and hydrophobic PVC. More water residential sites consumed more water with increasing wood content. The thickness swelling of A1 composites increased from 1.54% after 2 h to 3.41% after 24 h, 9.50% after 168 h, 14.52% after 336 h, 15.61% after 672 h, and 16.96% after 1008 h. The swelling of A2 composite was 1.37% after 2 h, 3.20% after 24 h, 7.84% after 167 h, 12.96% after 336 h, 13.98% after 672 h, and 14.19% after 1008 h. A5 has the lowest thickness swelling value of 0.57% after 2 h, 0.85% after 24 h, and then a constant value of 1.14% after 168 h until 1008 h due to lack of encapsulated filler of OPF and fine PBCC in a PVC matrix that shows no noticeable changes in the composite microstructure.

3.7. Specific Gravity (Sp.gr.). The influence of OPF and PBCC contents on the specific gravity of composites is explained in Table 11. The sp.gr. values of A0 and A1 composites were 1.44 and 1.40. The sp.gr. of A1 was not significantly affected because
Figure 6. SEM images of fracture surfaces of A1, A2, and A5 composites.

Table 6. Tensile Strength, Tensile Modulus, and Strain at Break of PVC and Its Composites\(^a\)

| Sample | Tensile Strength (MPa) | Tensile Modulus (MPa) | Strain at Break (%) |
|--------|------------------------|-----------------------|---------------------|
| A0     | 41.76(0.68)            | 1168(6.87)            | 87.42(0.08)         |
| A1     | 22.78(0.84)            | 1455(9.77)            | 2.97(0.03)          |
| A2     | 29.21(0.53)            | 2196(56.97)           | 3.11(0.01)          |
| A3     | 24.14(0.25)            | 1837(6.87)            | 3.20(0.05)          |
| A4     | 21.06(0.29)            | 1689(9.07)            | 3.36(0.49)          |
| A5     | 20.85(0.44)            | 1617(13.47)           | 3.65(0.15)          |

\(^a\)Means with same letters in the same column are not significant, difference at 5% level of probability according to the LSD test.

Table 7. Izod Impact Resistance of PVC/OPF/PBCC Composites

| Code Samples | Notched Izod Impact Strength (J/m), LSD\(_{\alpha=0.05}\) = 1.08 |
|--------------|-------------------------------------------------------------|
| A0           | 84.5(0.47)                                                  |
| A1           | 44.62(0.26)                                                 |
| A2           | 54.10(0.08)                                                 |
| A3           | 46.98(0.73)                                                 |
| A4           | 45.32(0.27)                                                 |
| A5           | 49.75(0.46)                                                 |

\(^a\)Means with same letters in the same column are not significant, difference at 5% level of probability according to the LSD test.

Table 8. Flexural Strength of PVC/OPF/PBCC Composites

| Code Samples | Flexural Strength (MPa), LSD\(_{\alpha=0.05}\) = 0.38 |
|--------------|-----------------------------------------------------|
| A0           | 78.68(0.22)                                         |
| A1           | 44.74(0.23)                                         |
| A2           | 51.89(0.26)                                         |
| A3           | 45.53(0.12)                                         |
| A4           | 44.85(0.19)                                         |
| A5           | 49.56(0.20)                                         |

Table 9. Shore-D Hardness of PVC/OPF/PBCC Composites\(^a\)

| Code Samples | Shore-D Hardness, LSD\(_{\alpha=0.05}\) = 2.03 |
|--------------|------------------------------------------------|
| A0           | 76(0.55)                                          |
| A1           | 79(0.56)                                          |
| A2           | 82(0.8)                                           |
| A3           | 83(1.97)                                          |
| A4           | 85(1.12)                                          |
| A5           | 86(1.12)                                          |

\(^a\)Means with same letters in the same columns are not significant, difference at 5% level of probability according to the LSD test.

OPF has less bulk density than PVC. Sp.gr. increased by adding PBCC in more than 10% that may be due to the higher bulk density of PBCC than PVC. The sp.gr. values of A2, A3, A4, and A5 are 1.42, 1.58, 1.61, and 1.88, respectively. From A1 to A5, the weight of PBCC filler increased the matrix density.\(^30\)

3.8. Thermal Characteristics. The TGA curves of A0, A1, A2, A3, A4, and A5 samples are listed in Table 12. The TGA curve for A0 has two weight loss stages in the range of 257° to 372°C by 54.6% due to H−Cl elimination reaction and formation of polyene. Chlorine radicals are liberated from C−Cl bond scission taking off hydrogen radical from the adjacent C−H to produce the H−Cl bond. Such a mechanism generates double bonds in the polymer.\(^48\) It develops via the chain according to the fact that every unsaturated bond dislocates the (Cl) atom in position with “allyl” activation resulting in H−Cl affecting the thermal stability without losing weight from 372 to 420°C. Conjugated double bonds were obtained and a formed polyacetylene was more heat-stable than PVC because of cross-linking after forming. The second loss stage at 420°−500°C is much shorter than the first one corresponding to polyacetylene cracking. There are three stages of A1, A2, A3, and A4 composites decomposition. The first one is related to H₂O vaporization between 25.7 and 125°C with weight losses of 5.9% for A1, 5.3% for A2, 4.5% for A3, and 3.3% for A4. This decrease in weight in this stage is related to the decrease in OPF content. Composites start to decompose after water vaporization at the second stage in the range of 238−372°C for A1 with a weight loss of 55.8%, 240−372°C for A2 with a weight loss of 51.6%, 243−372°C for A3 with weight loss of 45.8%, and 244−372°C for A4 with a weight loss of 38.9%. Composites begin to decompose at stage 3, which starts from 370 to 500°C with weight loss of 17.9% for A1, 15.4% for A2, 16.2% for A3, and 12.5% for A4. The TGA curve of the A5 composite has three stages. The first stage starts in the range of 25.7−125°C with a small weight loss of 1.5% due to the absorbed moisture. The second stage starts in the range of 246−357°C with a weight loss of 21.9%, and the third stage starts in the range of 357−500°C with a weight loss of 11.6%. In the range of 372−460°C, the formed polyacetylene is more stable than PVC and hemicellulose decomposed, so the weight loss is observed for PVC/...
OPF composites, leaving a stable PVC in this temperature range.\textsuperscript{49,50} In this range of temperature, organic impurities in PBCC may decompose while the PVC compound remains stable. The onset of decomposition temperature of the PVC compound decreased with the addition of either OPF or PBCC. This is because of the filler content inducing defects in the form of aggregates and heterogeneities in the polymer matrix. The decomposition onset temperatures for A2, A3, A4, and A5 composites were lower than that of neat PVC. The thermal stability of such composites is enhanced because of the small particles size of PBCC compared with OPF particle size and the total surface contact area of PBCC particles/PVC matrix is more than that of OPF particles/PVC matrix. The PVC matrix can be protected from heat, and PBCC may act as an acid acceptor adding stabilization for PVC and neutralization of Cl\textsuperscript{−}. PBCC has a high surface area because of small particle size.

The most important temperature-dependent property for amorphous polymers is the glass-transition temperature (\(T_g\)), the temperature at which the polymer changes from a relatively brittle material to a softer plastic material, which was determined by differential scanning calorimetry (DSC). The DSC curves in Figure 8 showed \(T_g\)'s of A0, A1, A2, A3, A4, and A5 at 85, 92.3, 93.7, 92.8, 91.9, and 92.8 °C, respectively. The increase of \(T_g\) after adding OPF may be due to the polar–polar interactions between PVC and olive pits flour molecules forming strong hydrogen bonds, which prohibit the chain mobility. In addition, the homogeneous distribution of PBCC in the PVC matrix is the driving force that increases the \(T_g\) of the PVC/PBCC composites prohibiting the molecular chain movement of PVC.\textsuperscript{13}

Table 10. Water Absorption % of PVC/OPF/PBCC Composites\textsuperscript{a}

| sample | 2 h | 24 h | 168 h | 336 h | 672 h | 1008 h |
|--------|-----|------|-------|-------|-------|-------|
| A0     | 0.13\textsuperscript{a} (0.007) | 0.15\textsuperscript{a} (0.001) | 0.22\textsuperscript{a} (0.002) | 0.37\textsuperscript{a} (0.087) | 0.38\textsuperscript{a} (0.087) | 0.38\textsuperscript{a} (0.085) |
| A1     | 1.76\textsuperscript{a} (0.018) | 4.22\textsuperscript{b} (0.242) | 10.79\textsuperscript{b} (0.001) | 14.33\textsuperscript{b} (0.164) | 15.07\textsuperscript{b} (0.052) | 15.68\textsuperscript{b} (0.105) |
| A2     | 1.18\textsuperscript{b} (0.017) | 3.15\textsuperscript{b} (0.112) | 8.24\textsuperscript{b} (0.135) | 11.21\textsuperscript{b} (0.011) | 11.64\textsuperscript{b} (0.318) | 12.28\textsuperscript{b} (0.521) |
| A3     | 1.08\textsuperscript{b} (0.087) | 2.91\textsuperscript{b} (0.102) | 8.03\textsuperscript{b} (1.003) | 8.85\textsuperscript{c} (0.888) | 8.94\textsuperscript{c} (0.499) | 9.24\textsuperscript{c} (0.082) |
| A4     | 0.94\textsuperscript{b} (0.037) | 2.52\textsuperscript{b} (0.249) | 6.86\textsuperscript{b} (1.005) | 8.52\textsuperscript{b} (0.231) | 8.73\textsuperscript{c} (0.025) | 8.86\textsuperscript{c} (0.138) |
| A5     | 0.31\textsuperscript{b} (0.009) | 0.37\textsuperscript{b} (0.007) | 0.46\textsuperscript{b} (0.035) | 0.74\textsuperscript{b} (0.058) | 0.75\textsuperscript{b} (0.058) | 0.75\textsuperscript{b} (0.057) |

\textsuperscript{a}Means with same letters in the same column are not significant, difference at 5% level of probability according to the LSD test.

Table 11. Specific Gravities of the Prepared Composites\textsuperscript{a}

| code samples | Sp.gr., LSD\textsubscript{0.05} = 0.18 |
|--------------|---------------------------------|
| A0           | 1.44\textsuperscript{b} (0.01) |
| A1           | 1.40\textsuperscript{b} (0.02) |
| A2           | 1.42\textsuperscript{b} (0.02) |
| A3           | 1.58\textsuperscript{b} (0.01) |
| A4           | 1.61\textsuperscript{b} (0.02) |
| A5           | 1.88\textsuperscript{a} (0.01) |

\textsuperscript{a}Means with same letters in the same column are not significant, difference at 5% level of probability according to the LSD test.

OPF composites, leaving a stable PVC in this temperature range.\textsuperscript{49,50} In this range of temperature, organic impurities in PBCC may decompose while the PVC compound remains stable. The onset of decomposition temperature of the PVC compound decreased with the addition of either OPF or PBCC. This is because of the filler content inducing defects in the form of aggregates and heterogeneities in the polymer matrix. The decomposition onset temperatures for A2, A3, A4, and A5 composites were lower than that of neat PVC. The thermal stability of such composites is enhanced because of the small particles size of PBCC compared with OPF particle size and the total surface contact area of PBCC particles/PVC matrix is more than that of OPF particles/PVC matrix. The PVC matrix can be protected from heat, and PBCC may act as an acid acceptor adding stabilization for PVC and neutralization of Cl\textsuperscript{−}. PBCC has a high surface area because of small particle size.

The most important temperature-dependent property for amorphous polymers is the glass-transition temperature (\(T_g\)), the temperature at which the polymer changes from a relatively brittle material to a softer plastic material, which was determined by differential scanning calorimetry (DSC). The DSC curves in Figure 8 showed \(T_g\)'s of A0, A1, A2, A3, A4, and A5 at 85, 92.3, 93.7, 92.8, 91.9, and 92.8 °C, respectively. The increase of \(T_g\) after adding OPF may be due to the polar–polar interactions between PVC and olive pits flour molecules forming strong hydrogen bonds, which prohibit the chain mobility. In addition, the homogeneous distribution of PBCC in the PVC matrix is the driving force that increases the \(T_g\) of the PVC/PBCC composites prohibiting the molecular chain movement of PVC.\textsuperscript{13}

Table 12. Decomposition Stages and Weight Loss of PVC/OPF/PBCC

| decomposition stage | first | second | third | total residue (%) at temp. 500 °C |
|---------------------|-------|--------|-------|----------------------------------|
| composites          | start (°C) | end (°C) | wt loss (%) | start (°C) | end (°C) | wt loss (%) | total residue (%) |
| A0                  | 257   | 372   | 54.6   | 420   | 500   | 12.46   | 32 |
| A1                  | 25.7  | 125   | 5.9    | 238   | 372   | 55.8    | 372 | 5500 | 17.9    | 20.4 |
| A2                  | 25.7  | 125   | 5.3    | 240   | 372   | 51.6    | 372 | 5500 | 15.4    | 27.7 |
| A3                  | 25.7  | 125   | 4.5    | 243   | 372   | 45.8    | 372 | 500  | 16.2    | 33.5 |
| A4                  | 25.7  | 125   | 3.3    | 244   | 372   | 38.9    | 372 | 500  | 12.5    | 45.3 |
| A5                  | 25.7  | 125   | 1.5    | 246   | 357   | 21.9    | 357 | 500  | 11.6    | 65 |

Means with same letters in the same column are not significant, difference at 5% level of probability according to the LSD test.
4. CONCLUSIONS

For keeping the environment clean, low-cost wastes olive pits flour and precipitated bio-calcium carbonate were successfully used as fillers in PVC. The formed composites have superior thermal stability, stiffness, and physical and mechanical properties compared to PVC. The uniform distribution of PBCC in the PVC/OPF composite is a major factor responsible for the improvement of most properties. In the future work, different ways may be investigated to improve the PBCC dispersion at higher contents than 10 wt% aiming to decrease the cost of processing such composites.

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Notes
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■ REFERENCES

(1) Ali, S. F. A. Biodegradation properties of poly-ε-caprolactone, starch and cellulose acetate butyrate composites. J Polym. Environ. 2014, 22, 359–64.
(2) Abdellah-Ali, S. F. Mechanical and thermal properties of promising polymer composites for food packaging applications. In IOP Conference Series: Materials Science and Engineering; IOP Publishing, 2016; Vol. 137, p 012035.
(3) Abdellah-Ali, S. F.; Hassan, W. K. Investigation and Evaluation of Poly (n-butyl acrylate) for Oil Fractions Spill Removal Applications. Egypt. J. Chem. 2020, 63, 15–25.
(4) Abdellah-Ali, S. F. Performance of cellulose acetate propionate in polycaprolactone and starch composites: biodegradation and water resistance properties. Biointerface Res. Appl. Chem. 2020, 10, 5382–6.
(5) Migneault, S.; Koubaa, A.; Erchiqui, F.; Chaala, A.; Englund, K.; Wolcott, M. P. Effects of processing method and fiber size on the structure and properties of wood–plastic composites. Composites, Part A 2009, 40, 80–5.
(6) El-Rafey, E.; Walid, W. M.; Syala, E.; Ezrat, A. A.; Abdellah-Ali, S. F. A study on the physical, mechanical, thermal properties and soil biodegradation of HDPE blended with PBS/HDPE-g-MA. Polym. Bull. 2021, 175, No. 109126.
(7) Abd El-Rahman, K. M.; Abdellah Ali, S. F.; Khalil, A. I.; Kandil, S. Influence of poly(butylene succinate) and calcium carbonate nano-
particles on the biodegradability of high-density-polyethylene nanocomposites. *J Polym Res.* **2020**, *27*, No. 231.

(8) Abdellah-Ali, S. F. Performance of cellulose acetate propionate in polycaprolactone and starch composites: biodegradation and water resistance properties. *Biointerface Res. Appl. Chem.* **2020**, *10*, S382–6.

(9) Ali, S. F. A.; Elsad, R. F.; Mansour, S. A. Enhancing the dielectric properties of compatibilized high-density polyethylene/calcium carbonate nanocomposites using high-density polyethylene-g-maleic anhydride. *Polym. Bull.* **2021**, *78*, 1393–405.

(10) Fink, J. K. *Acoustic Introduction to Additives for Thermoplastic Polymers*, 1st ed.; John Wiley & Sons, 2010; Vol. 1.

(11) Stuart, P. *PVC Compounds and Processing*; Rapra Technology Limited: United Kingdom, 2004; Vol. 15.

(12) Xu, Y.; Wu, Q.; Lei, Y.; Yao, F.; Zhang, Q. Natural fiber reinforced poly (vinyl chloride) composites: Effect of fiber type and impact modifier. *J. Polym. Environ.* **2008**, *16*, 250–7.

(13) Abdellah-Ali, S. F.; Mervette, E. B.; Abdelhamed, M.; El-Rafei, E. Formulation and characterization of new ternary stable composites: Polyvinyl chloride-wood flour-calcium carbonate of promising physicochemical properties. *J. Mater. Res. Technol.* **2020**, *9*, 12840–12854.

(14) Titow, M. V. *PVC Technology*; Springer Science & Business Media, 2012.

(15) Mishra, S. B.; Mishra, A. K.; Kaushik, N. K.; Khan, M. A. Study of performance properties of lignin-based polyl e ngs with polyvinyl chloride. *J. Mater. Process. Technol.* **2007**, *183*, 273–276.

(16) Gilbert, M.; Patrick, S. Poly(vinyl chloride); Brydon’s Plastics Materials, 2017; pp 1–18.

(17) Lietke, E. Recent Developments of PVC Compounds for Special Applications. In *PVC-Formulation Conference (AMI)*, Cologne, Germany, 2009.

(18) Jariwala, H.; Jain, P. A review on mechanical behavior of natural fiber reinforced polymer composites and its applications. *J. Rein. Plast. Compos.* **2019**, *38*, 441–53.

(19) Joshi, P. S.; Marathe, D. S. Mechanical properties of highly filled PVC/wood-flour composites. *J. Rein. Plast. Compos.* **2010**, *29*, 2522–33.

(20) Yañez-Pacios, A. J.; Martín-Martínez, J. M. Surface modification and adhesion of wood-plastic composite (WPC) treated with UV/ozone. *Compos. Interfaces* **2018**, *25*, 127–149.

(21) Zhou, Y.; Fan, M.; Chen, L. Interface and bonding mechanisms of plant fibre composites: An overview. *Composites, Part B* **2016**, *101*, 31–45.

(22) Altun, Y.; Doğan, M.; Bayramli, E. Comparative study of maleated and glycidyl methacrylate functionalized terpolymers as compatibilizers for low-density polyethylene—wood flour composites. *J. Appl. Polym. Sci.* **2013**, *127*, 1010–1016.

(23) Matuana, L. M. Recent developments in wood polymer composites. *J. Vinyl Addit. Techn.* **2009**, *15*, 136–138.

(24) Sombatsompop, N.; Prapruen, W.; Chaochanthachkul, K.; Pulgern, T.; Rosaripatik, V. Effects of cross section design and testing conditions on the flexural properties of wood/PVC composite beams. *J. Vinyl Addit. Techn.* **2010**, *16*, 33–41.

(25) Bahari, S. A.; Warren, J. G.; Andreas, K. Thermal stability of processed PVC/bamboo blends: effect of compounding procedures. *Eur. J. Wood Prod.* **2017**, *75*, 147–159.

(26) Gozdecki, C. E.; Wilczynski, A. Effect of Wood Flour Type on Tensile Properties of Wood-Polymer Composites; Annals of Warsaw University of Life Sciences-SGGW. Forestry and Wood Technology, 2015; Vol. 91.

(27) Najafi, S. K. Use of recycled plastics in wood plastic composites—A review. *Waste Manag.* **2013**, *33*, 1899–905.

(28) Dairi, B.; Dijdjelli, H.; Boukerrou, A. Study and characterization of composites materials based on polyvinyl chloride loaded with wood flour. *J. Mater. Sci. Eng. A* **2013**, *3*, 110–116.

(29) Farshbehi, A. T.; Taleiopour, M.; Hemmasi, A. H.; Khademislem, H.; Ghasemi, I. Investigation on the mechanical and morphological properties of foamed nanocomposites based on wood flour/PVC/multi-walled carbon nanotube. *Bioresources* **2011**, *6*, 841–52.

(30) Azwa, Z. N.; Yousif, B. F.; Manalo, A. C.; Karunasena, W. A review on the degradability of polymeric composites based on natural fibres. *Mater. Des.* **2013**, *47*, 424–42.

(31) Ashori, A. Wood–plastic composites as promising green-composites for automotive industries. *Bioresour. Technol.* **2008**, *99*, 4661–7.

(32) John, M. J.; Thomas, S. Biofibres and biocomposites. *Carbohydr. Polym.* **2008**, *71*, 343–64.

(33) Cornell, D. W. Benefits of PCC as a PVC Additive. In Third Minerals in Compounding Conference, Cologne, Germany, pp 35–37, 2001.

(34) Guffey, V. O.; Sabbagh, A. B. PVC/wood-flour composites compatibilized with chlorinated polyethylene. *J. Vinyl Addit. Techn.* **2002**, *8*, 259–263.

(35) Chen, Y.; Chiparus, O.; Sun, L.; Negulescu, I.; Parikh, D. V.; Calamari, T. A. Natural fibers for automotive nonwoven composites. *J. Ind. Text.* **2005**, *35*, 47–67.

(36) Rowell, D. L. *Soil Science: Methods & Applications*; Routledge, 2014.

(37) Saini, G.; Choudhary, V.; Bhardwaj, R.; Narula, A. K. Study on PVC composites containing Eugenia jambolana wood flour. *J. Appl. Polym. Sci.* **2008**, *107*, 2171–2179.

(38) Yannm, C.; Jangung, L.; Meng, Z.; Wen, Z.; Yong, L.; Zhaohong, W.; Jimin, F. Discrimination of Carbonate-Containing and Calcium-Free Polyvinyl Chloride with Fourier Transform Infrared Microscopy and Raman Spectroscopy. *Spectroscopy* **2012**, *27*, 36–41.

(39) Yang, Z.; Yang, H. Effects of sucrose addition on the rheology and microstructure of k-carrageenan gel. *Food Hydrocollids* **2018**, *75*, 164–73.

(40) Bai, X. Y.; Wang, Q. W.; Sui, S. J.; Zhang, C. S. The effects of wood-flour on combustion and thermal degradation behaviors of PVC in wood-flour/poly (vinyl chloride) composites. *J. Anal. Appl. Pyrolysis* **2011**, *91*, 34–9.

(41) Liu, P.; Zhao, M.; Guo, J. Thermal stabilities of poly (vinyl chloride)/calcium carbonate (PVC/CaCO3) composites. *J. Macromol. Sci., Part B: Phys.* **2006**, *45*, 1135–40.

(42) Bouhamed, N.; Souissi, S.; Marechal, P.; Amor, M. B.; Lenoir, O.; Leger, R.; Bergeret, A. Ultrasound evaluation of the mechanical properties as an investigation tool for the wood-polymer composites including olive wood flour. *Mech. Mater.* **2020**, *148*, No. 103445.

(43) Kemal, I.; Whittle, A.; Burford, R.; Vodenitcharova, T.; Hoffman, M. Toughening of unmodified polyvinylchloride through the addition of nanoparticulate calcium carbonate. *Polymer* **2009**, *50*, 4066–79.

(44) Ramli, R. A.; Zakaria, N. Z.; Rahman, U. U.; Bakhitri, N. B.; Mustapha, S. N.; Lian, Y. M. Effect of mineral fillers on mechanical, thermal and morphological properties of kenaf recycled polyethylene wood plastic composite. *Eur. J. Wood Prod.* **2018**, *76*, 1737–43.

(45) Shojaeiarian, J.; Bajwa, D. S.; Stark, N. M. Green esterification: A new approach to improve thermal and mechanical properties of poly (lactic acid) composites reinforced by cellulose nanocrystals. *J. Appl. Polym. Sci.* **2018**, *135*, 46468.

(46) Michael, A. *Materials Selection in Mechanical Design Book*, 4th ed.; Elsevier-India, 2011.

(47) Ashori, A.; Nourbakhsh, A. Performance properties of microcrystalline cellulose as a reinforcing agent in wood plastic composites. *Composites, Part B* **2010**, *41*, 578–581.

(48) Akay, M. *Introduction to Polymer Science and Technology*; Ventus Publishing Aps: N. Ireland, 2012.

(49) Pioletto, M.; Zattera, A. J.; Forte, M. M.; Santana, R. M. Thermal decomposition of wood: Influence of wood components and cellulose crystallite size. *Bioresour. Technol.* **2012**, *109*, 148–153.

(50) Fang, Y.; Wang, Q.; Bai, X.; Wang, W.; Cooper, P. A. Thermal and burning properties of wood flour-poly (vinyl chloride) composite. *J. Therm. Anal. Calorim.* **2012**, *109*, 1577–85.