Enhanced thermal and mechanical properties by cost-effective carboxylated nanodiamonds in poly (vinyl alcohol)

Yuansai Zhanga,b, Qingsong Huab,c, Jian Min Zhanget al.

ABSTRACT
In this study, the high-energy ball-milled nanodiamonds (MNDs) are carefully treated with low-temperature annealing and mixed acids to obtain carboxylated MNDs (cMNDs). This process not only removes impurities but also grafts oxygen containing functional groups onto MNDs surfaces. Then poly (vinyl alcohol) (PVA)/cMND nanocomposites are prepared by a facile aqueous solution casting method. Compared with PVA/MND, an improved dispersion of nanoparticles in the matrix and higher nanoparticles content can be achieved by PVA/cMND. It is found that glass transition temperature ($T_g$) and loss factor peak temperature ($\tan \delta$) of PVA/cMND nanocomposites are both shifted to higher values than pure PVA. Thermal decomposition of PVA is obviously suppressed by cMNDs. The onset and maximum decomposition temperatures increases by over 17 $^\circ$C and 24 $^\circ$C, respectively. The thermal conductivity increases by 57.5%. Furthermore, tensile strength and Young’s modulus of PVA are improved by 62.3% and 166.7% with the addition of cMNDs.

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1. Introduction
Nowadays, polymer materials have been used in a broad range of engineering industries, such as aviation, sport products, automobile, and electronic devices. Such applications are utilizing the advantageous features of polymer materials in light-weight, electrical insulation, tribological properties, and flexibility, etc. However, native polymer materials exhibit limited mechanical properties due to its flexible carbon backbone chains and weak Van der Waals forces between polymer chains. To further improve mechanical properties, micro-sized reinforcing fibers (e.g. carbon or glass fiber) are often added into polymer matrix to obtain polymer composites with higher mechanical properties. Recently, with the development of nanomaterials, the addition...
of nanofillers (e.g. carbon nanotube [1, 2], carbon nanofiber [3, 4], nanoclay [5], cellulose nanofiber [6], graphene [7–11]) in polymer matrix have been extensively studied in both academia and industry because nanofillers can achieve similar or superior reinforcing effects in polymer matrix to their micro-sized counterparts but at a much lower loading level. Thus, the advantages of polymer materials such as processability and lightweight can be substantially retained in these nanocomposites. Besides mechanical performance, one or more functionalities such as electrical or thermal properties, flame retardancy, and recyclability can be greatly enhanced by the addition of suitable nanofillers. However, it is still difficult for these nanocomposites to achieve anticipated properties, which is mainly due to nanofillers aggregation and poor interface between nanofillers and polymer matrix [9].

Nanodiamond (ND) is a kind of zero-dimensional nanofillers with a spherical-like structure, and dimensions ranging from few nanometers to few hundred nanometers. Three commercially available production methods for ND have been developed so far, i.e. detonation, laser ablation, and high-energy ball milling of high-pressure high-temperature diamond microcrystals, which makes ND relatively cheaper carbon nanomaterials [12]. Since its first large-scale production by detonation process in 1960s, plenty attention has been attracted by ND thanks to their outstanding physical properties such as high thermal conductivity, superb bulk modulus, friction resistance. Currently, their applications include polishing materials, sensors, supporters for catalysts and nanocomposites. So far, several polymer/ND composites have been investigated, including epoxy/ND [13–16], polyimide/ND [17, 18], poly(lactic acid)/ND [19, 20], and poly(vinyl alcohol)/ND [21, 22]. Mochalin et al. [15] synthesized aminated ND particles to covalently incorporate into the epoxy polymer network, which led to 50% higher Young’s modulus compared to epoxy/ND composites with no covalent linkage. Acid treated ND was utilized to prepare PVA/ND nanocomposites by Maitra et al. [21], showing that even at a low ND loading (up to 0.6 wt%) remarkable improvement on the mechanical and thermal properties can be achieved. Although various surface functionalization approaches have been developed to enhance the interaction between ND and polymer matrix in a molecular level, the dispersion of ND particles in polymer matrix are still difficult to control.

To date, the effectiveness of ND as nanofiller in polymer matrix has been less studied than other carbon nanomaterials. In addition, polymer/ND nanocomposites are mostly prepared with ND from detonation process (named as DND). ND which is produced by high-energy ball-milling technique (named as MND) as nanofillers in polymer matrix have rarely been studied in the literature. The inexpensive MND (only cost one tenth of DND price) exhibit an average particle size of 50 nm, which is one order of magnitude larger than DND (∼ 5 nm), therefore, they show less tendency to aggregate into clusters than DNDs. It is expected that more homogenous dispersion and better reinforcing effect can be realized by these low cost MNDs with a suitable surface treatment.

In this study, we carefully treated MNDs by low-temperature annealing and mixed acids to obtain carboxylated MNDs (cMNDs) and later on prepared PVA/cMND nanocomposites by a facile solution casting method. Different from previous research in PVA/ND nanocomposites [22], the purpose of this study is to systematically investigate and compare the reinforcing effect of the MNDs and cMNDs on the thermal and mechanical properties of these nanocomposites. By means of various characterization methods such as Fourier transform infrared spectrum (FTIR), field emission scanning electronic microscopy (FE-SEM), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimeter analysis (TGA) and tensile tests, surface chemistry, morphology, crystallinity, thermal, and mechanical properties of these nanocomposites were examined and discussed in detail.

2. Experimental

2.1. Materials

MND powders synthesized by high-energy ball-milling process from diamond microcrystals were provided by Yuxing Sino Crystal Micron Diamond Co., Ltd. (He Nan, China). Polyvinyl alcohol (PVA 1788) was purchase from Aladdin Co., Ltd, degree of saponification is 88% and degree of polymerization is 1700. Concentrated nitric acid (68%) and sulfuric acid (98%) were purchased from Zhitang Fine Chemicals Co., Ltd. (Jiangsu, China).

2.2. Sample preparation

MND powders were first oxidized at 425 °C for five hours in a furnace to remove amorphous and graphitic carbon content on the surface of MNDs. Then the oxidized MNDs were refluxed with the mixture of sulfuric acid and nitric acid (\(V_{H_2SO_4}:V_{HNO_3} = 3:1\)) at 120 °C in a reflux condensation equipment for 48 h. The resulting carboxylated MNDs (cMNDs) were extensively rinsed with deionized water. Then the cMNDs were dried in a vacuum oven at 80 °C for 24 h. The basic formation of the hydroxyl, carbonyl and carboxylation groups on
the cMNDs by this carboxylation process can be formulated by the following Equation (1) [23].

\[
\text{C} + \text{HNO}_3 \xrightarrow{+\text{H}_2\text{O}} \text{C} = \text{O} = \text{NO}_2 \xrightarrow{-\text{HNO}_3} \text{C} - \text{OH} \xrightarrow{\text{oxidation}} \text{O} = \text{C} - \text{OH}
\]

\[(1)\]

For preparing PVA/MND and PVA/cMND nanocomposites, PVA powders were completely dissolved in hot deionized water at 90°C by vigorously stirring for two hours. The MNDs or cMNDs were dispersed in water and ultrasonicated for one hour at 65 W output power. Then MNDs or cMNDs aqueous suspension was added into PVA solution, to achieve a better dispersion, the mixture was stirred for another one hour. The PVA/MND or PVA/cMND suspension was cast into a petri-dish and dried at room temperature and then dried at 40°C in a vacuum oven for 24 h. The nanocomposite films with 0.5, 1, 2, 3, and 10 wt% contents in PVA matrix were then successfully prepared. The samples have a controlled thickness of 400 μm. All the samples were kept in a desiccator before any characterization tests.

2.3. Characterization

FTIR was recorded on a FTIR spectrophotometer (Bruker Tensor 27, Germany) using the KBr method. The resolution was 4 cm\(^{-1}\). A field emission scanning electronic microscopy (FE-SEM) (JSM-7800F, Japan) was used to investigate the morphology of nanocomposites. Specimens were coated with gold and backscattering imaging mode was used.

WAXD measurements were performed on the samples. The monochromatized Cu K\(\alpha\) radiation generated by a Rigaku D/MAX-RB diffractometer (Japan) (40 mV, 40 mA) was irradiated on specimen perpendicular to the surface. The diffraction profile was detected using an X-ray goniometer with symmetric reflection geometry. Diffraction profiles were resolved into noncrystalline scattering and crystalline reflections using Rigaku multi-peaks separation software.

DSC measurements were performed using a Mettler-Toledo DSC1 (Switzerland), at a constant annealing and cooling rate of 20°C-min\(^{-1}\). DMA was performed using a Perkin Elmer DMA 8000 (USA). Uniaxial specimens with a gauge length of 11 mm were subjected to sinusoidal tensile displacement with a controlled strain of 0.06 mm at a frequency of 10 Hz and temperatures ramped from 0°C to 150°C at a rate of 6°C-min\(^{-1}\). TGA was performed using Mettler-TGA/DSC1SF (Switzerland). An annealing rate of 20°C/min was employed under nitrogen flow and the sample chambers were heated from 50°C to 400°C. Thermal conductivity measurements were carried out on PVA, PVA/MND and PVA/cMND nanocomposites with different nanoparticle contents. The measurements were conducted on circular film samples \((D = 12.7 \text{ mm})\) at 25°C using a NETZSCH LFA447 light flash system (Germany).

Tensile tests were carried out on an Instron 5500R tensile testing machine (USA). Gauge length was 20 mm and cross-head speed was 2.0 mm-min\(^{-1}\).

3. Results and discussion

3.1. FTIR analysis

It is suggested that a good dispersion of nanoparticles in polymer matrix can be attribute to various functional groups on their surfaces. To further characterize the changes of functional groups after MNDs carboxylation process, the FTIR spectrums of MNDs and cMNDs were obtained, as showed in Figure 1. According to the spectrum (a), the peak around 3394 cm\(^{-1}\) can be assigned to the characteristic peak of the stretching vibrations of the hydroxyl groups [24]. The peak around 1443 cm\(^{-1}\) is the stretching and deformation vibrations of alkyl groups [22]. The peak around 1785 cm\(^{-1}\) is assigned to the stretching vibration of C=O for the carboxyl groups [25]. The peak around 1094 cm\(^{-1}\) can be assigned to the stretching vibration of C−O for the ethers [26]. The absorption peak at 1625 cm\(^{-1}\) can

Figure 1. FTIR spectrums of (a) MND and (b) cMND.

Figure 2. An illustration of hydrogen bonding between cMNDs and PVA molecules.
be assigned to the blending vibrations of the hydroxyl groups and stretching vibration of aromatic sp² carbon bond related to graphite structure [27]. The spectrum (b) shows that the peaks of C=O and the O–H were significantly enhanced. It means more carboxyl groups and hydroxyl groups were grafted onto the cMNDs surfaces during the carboxylation process. These oxygen-containing functional groups (carboxyl, hydroxyl, and others) can suppress the aggregation of cMNDs by the electrostatic repulsion [28]. Furthermore, the interfacial interactions between PVA and cMNDs can be improved by hydrogen bonding formed between these oxygen-containing functional groups and hydroxyl groups on PVA molecules, as shown in Figure 2.

3.2. Morphology

The morphology of MNDs, PVA/MND and PVA/cMND nanocomposites were investigated by field emission-scanning electron microscopy (FE-SEM) (Figure 3). It is indicated in Figure 3(a) that MNDs in this study exhibit a range of dimensions from ~20 nm to ~100 nm. There are MNDs with dimension \( D = 50 \) nm, which is highlighted in the photograph as #1; The MNDs with \( D < 50 \) nm and \( D > 50 \) nm are shown as #2 and #3, respectively. It can be seen in Figure 3(b), 1 wt% MNDs were well dispersed inside the PVA matrix. When the MNDs content increased to 3 wt% and 10 wt%, lots of micro-scaled MNDs clusters were formed (Figure 3(c,e)) which suggests worse dispersion when MNDs content increased. Compared with Figure 3(c), carboxylated MNDs with the same weight content had a much better dispersion in PVA matrix (Figure 3(d)). Even at 10 wt% content, Figure 3(f) still shows a relatively homogeneous dispersion of cMNDs in the matrix. Therefore, by combining the results of FTIR and SEM, it is clearly proved that the carboxylation process of MNDs can create more oxygen-containing functional groups on

Figure 3. FE-SEM photographs for (a) MNDs and nanocomposites with (b) 1 wt% MNDs; (c) 3 wt% MNDs; (d) 3 wt% cMNDs; (e) 10 wt% MNDs; (f) 10 wt% cMNDs.

Figure 4. XRD diffraction profiles: (a) MNDs and cMNDs; (b) PVA and PVA/MND nanocomposites with different MNDs contents; (c) PVA and PVA/cMND nanocomposites with different cMNDs contents; (d) calculated crystallinity for PVA at (101) and (202) peaks.
the surfaces of MNDs, and effectively facilitates the dispersion of nanoparticles in PVA matrix.

3.3. X-ray diffraction profiles and crystallinity

X-ray diffraction profiles for MNDs, cMNDs, pure PVA, PVA/MND, and PVA/cMND nanocomposites were illustrated in Figure 4. As shown in Figure 4(a), characteristic diffraction peaks at $2\theta = 43.9^\circ$ (111) and $2\theta = 75.3^\circ$ (220) were clearly shown in the diffraction profiles of both MNDs and cMNDs, which are associated with the sp$^3$ carbon structure in nanodiamonds. The crystallinity of PVA was calculated by an integration of designated peak areas under (101) and (202) diffraction peaks (Figure 4(d)). It is known from literature [29] that the agglomerated nanoparticles would hinder the crystallization of polymer matrix. It clearly shown in Figure 4(d), the crystallinity of PVA significantly increased by the addition of cMNDs and remained as high as 39% for PVA/cMND nanocomposites with 3 wt% cMNDs. However, the crystallinity for PVA/MND nanocomposite only increased up to 35% by adding 2 wt% MNDs and it dropped obviously to 25% with 10 wt% MNDs which is lower than the crystallinity of pure PVA. It is resulted from the apparent agglomeration of MNDs in PVA matrix (see Figure 3(c)) which may hinder PVA crystallization process during the preparation of PVA/MND nanocomposites. While for PVA/cMND nanocomposites, the crystallinity increased from 28% to 35% by increasing cMNDs content from 0% to 3 wt%. Even for 10 wt%, the crystallinity of PVA/cMND nanocomposites is still much higher than that of PVA/MND nanocomposites due to better dispersion of cMNDs in PVA matrix (Figure 3(e,f)).

3.4. Thermal properties

The thermal degradation behavior of pure PVA, PVA/MND, and PVA/cMND nanocomposites were investigated by thermogravimetry measurements. As shown in Figure 5(a), three distinct stages of mass loss can be observed from the thermogravimetric (TG) curves. The first stage of mass loss ($\sim$3 wt%) is considered to be the evaporation of water, which may be due to the hydroscopic nature of PVA and relatively insufficient drying process during sample preparation. The existence of water in the samples may cause a reduction in thermal properties and mechanical properties of both pure PVA and nanocomposites. The second stage of mass loss is due to the elimination reactions of PVA matrix and the third stage of mass loss is dominated by chain-scission and cyclization reactions [30]. The second stage of mass loss shows the major thermal degradation of PVA matrix. The onset temperature ($T_{onset}$) of thermal decomposition was calculated from an intersecting point of two tangential lines, the maximum decomposition temperature ($T_{max}$) was obtained from the first order derivative TG thermograph. As shown in Figure 5(a,b), the $T_{onset}$ and $T_{max}$ of the PVA/MND nanocomposites had no
obvious increase than pure PVA. However, the addition of cMNDs with the same weight content induced a significant increase in terms of \( T_{\text{onset}} \) and \( T_{\text{max}} \), revealing that the thermal decomposition of PVA was greatly suppressed by well dispersed cMNDs. It is proposed that the nanodispersed cMNDs can act as barriers to hinder the volatile decomposition of PVA matrix. Therefore, the PVA/cMND nanocomposites show better thermal stability compared with PVA/MND nanocomposites.

Thermal properties of PVA and PVA/MND nanocomposites were then characterized by differential scanning calorimetry (DSC) measurements. Figure 6(a) shows DSC endothermic curves for PVA and PVA/MND nanocomposite with different MND contents. In these DSC curves, the glass transition temperature \( (T_g) \) and melting temperature \( (T_m) \) did not change significantly with the addition of MNDs into PVA matrix. Figure 6(b) shows DSC endothermic curves for PVA and PVA/cMND nanocomposite with different cMND contents. We can find the \( T_g \) and \( T_m \) have been greatly improved compared to PVA/MND nanocomposites. The characteristic data derived from DSC endothermic curves were shown in Table 1. However, the values of \( T_g \) and \( T_m \) are lower than the common value of PVA, which may be because of the existence of water in the samples when drying process is not enough.

As shown in Table 1, the \( T_g \) and \( T_m \) of PVA/MND had no apparent increase even at 10 wt% loading. However, it is found that the \( T_g \) and \( T_m \) of PVA/cMND had more increase than PVA/MND. The \( T_g \) and \( T_m \) of PVA/cMND increased by 5 °C and 8 °C, respectively, compared with pure PVA. \( T_g \) is an indicating parameter for polymer molecule movement in the amorphous region, therefore, the increase in \( T_g \) can be explained that PVA chain movements in the amorphous region were suppressed by the strong hydrogen-bonding formed between cMNDs and PVA molecules [31]. It can be inferred from the above data that with a certain amount of cMNDs well-dispersed into PVA matrix, PVA/cMND nanocomposite could demonstrate suppressed molecular mobility in amorphous regions and increased molecular orientation in crystalline regions, which can, therefore, lead to better thermal stability.

The degree of crystallinity \( (C) \) of polymer can be calculated from DSC endothermic curves by Equation (2) when assuming a linear relationship between endothermal peak area and crystallinity:

\[
C = \frac{\Delta H}{\Delta H_0} \times 100\%
\]

where \( C \) is the crystallinity of a semicrystalline polymer, \( \Delta H \) is the heat of fusion of a semicrystalline polymer, \( \Delta H_0 \) is the heat of fusion of the 100% crystalline material, for PVA, which is 161 J/g. The calculated crystallinity is presented in Table 2. The absolute values of crystallinity calculated from DSC are not the same as those values calculated from XRD (Figure 4(d)) due to the elimination of thermal history in DSC measurements. However, the variation trend of crystallinity of PVA phase with increasing cMNDs weight concentration is in a good agreement.

Figure 7(a,b) show the effect of temperature on the dynamic mechanical properties of pure PVA, PVA/MND and PVA/cMND nanocomposites with 3 wt% loading. Similar to other semi-crystalline polymers, a decrease in storage modulus when increasing temperature was observed in all the samples. However, compared with pure PVA and PVA/MND, PVA/cMND nanocomposites can retain higher storage modulus at elevated temperatures. The temperatures at the tan \( \delta \) peak value \( (T_{\tan \delta}) \) for different samples were derived from Figure 7(b) and shown in Table 1. Generally, \( T_{\tan \delta} \) is associated with glass transition temperature \( T_g \) (\( \beta \) relaxation), which indicates molecule mobility in amorphous regions. With the addition of MNDs or cMNDs into PVA matrix, \( T_{\tan \delta} \) increases accordingly, which is in a good agreement with the \( T_g \) shown in DSC endothermic curves. Due to better dispersion and more hydrogen bonding with PVA molecules PVA/cMND exhibit a much higher \( T_{\tan \delta} \) than PVA/MND.

The thermal conductivity (\( \lambda \)) of PVA, PVA/MND and PVA/cMND with different nanoparticle contents were measured and shown in Figure 8. Higher thermal conductivity was achieved with increasing MND or cMND weight concentration in PVA matrix. The most common models used to demonstrate the thermal conductivity in a two-phase composite system are Maxwell’s in Equation (3).

### Table 1. The characteristic data derived from DSC.

| Samples          | \( T_g \) (°C) | \( T_m \) (°C) |
|------------------|----------------|----------------|
| PVA              | 68.5           | 183.2          |
| PVA/MND 0.5 wt%  | 70.6           | 178.5          |
| PVA/MND 1 wt%    | 70.2           | 182.4          |
| PVA/MND 2 wt%    | 70.1           | 183.5          |
| PVA/MND 3 wt%    | 70.0           | 182.5          |
| PVA/MND 10 wt%   | 71.2           | 182.0          |
| PVA/cMND 0.5 wt% | 71.8           | 189.2          |
| PVA/cMND 1 wt%   | 72.6           | 188.8          |
| PVA/cMND 2 wt%   | 73.4           | 187.5          |
| PVA/cMND 3 wt%   | 75.5           | 191.3          |
| PVA/cMND 10 wt%  | 74.8           | 190.6          |

### Table 2. The heat of fusion (\( \Delta H \)) and crystallinity (\( C \)) of PVA or PVA phase in the nanocomposites.

| Samples          | \( \Delta H \) (J/g) | \( C \) [%] |
|------------------|---------------------|-----------|
| PVA              | 39.76               | 25        |
| PVA/cMND 0.5 wt% | 41.66               | 26        |
| PVA/cMND 1 wt%   | 44.26               | 28        |
| PVA/cMND 2 wt%   | 48.56               | 30        |
| PVA/cMND 3 wt%   | 52.41               | 33        |
| PVA/MND 10 wt%   | 49.31               | 31        |
where $k_c$, $k_m$, and $k_f$ are the effective thermal conductivity of the composite, matrix, and filler. $V_f$ is the volume fraction of fillers in the composite. $k_m = 0.2 \, \text{W/(m·K)}$, $k_f = 2000 \, \text{W/(m·K)}$ [32], for PVA/MND composite with 3 wt% MNDs, $k_c$ is calculated to be 0.203 W/(m·K). The measured thermal conductivity for PVA/cMND nanocomposite with 3 wt% cMNDs reached to 0.315 W/(m·K), which increased by 57.5% than that of pure PVA and much higher than the calculated value. Various mechanisms of improved thermal conductivity of composites with nanofillers have been proposed by previous researchers [22]. It is proposed that the thermal conductivity of these nanocomposites is strongly dependent on the interfacial thermal resistance between polymer matrix and nanofillers. Due to the strong hydrogen-bonding between cMNDs and PVA, excellent interfacial properties would facilitate the formation of the heat transfer channel between cMNDs and PVA matrix, which is one of the reasons for a much better thermal conductivity of PVA/cMND than that of PVA/MND.

### 3.5. Mechanical behavior

Figure 9(a,b) shows the stress-strain curves of PVA, PVA/MND, and PVA/cMND nanocomposites. Pure PVA shows a typical stress-strain curve with low strength and an obvious long yielding behavior. We can find that the strain at failure for these nanocomposites was decreased with increasing MNDs or cMNDs weight concentration. However, PVA/cMND nanocomposites show much better toughness compared with PVA/MND nanocomposites. In Figure 9(c), it is found that both tensile strength and Young’s modulus increased when adding low weight concentration MNDs. The tensile strength and Young’s modulus reach a maximum of 41.6 MPa and 1.9 GPa when adding 1 wt% MNDs, however, the mechanical properties dropped significantly
when MND content increased beyond 2 wt%. While for the PVA/cMND nanocomposites (Figure 9(d)), the tensile strength and Young’s modulus reach a maximum of 56.3 MPa and 3.2 GPa with 3 wt% cMND content which improved by 63.2% and 167.7%, respectively, compared with those of neat PVA. This is mainly due to a good dispersion of cMNDs in PVA matrix even at higher weight concentrations, which can be proved by the morphological investigations in Figure 3. Meanwhile, better interfacial properties which were induced by more hydrogen bonds formed between PVA and cMNDs may facilitate the load transfer between the matrix and nanoparticles.

A simple ‘rule of mixture’ model is widely used to calculate the reinforcing efficiency of nanofillers in polymer nanocomposites. A predicted modulus of nanocomposites is given by Equation (4).

\[
E_c = E_m(1-V_f) + \eta E_f V_f
\]

where \(E_c\), \(E_m\), and \(E_f\) represent the Young’s modulus of the nanocomposites, matrix, and filler. \(V_f\) is the volume fraction of fillers in the composite, \(\eta\) is the filler’s reinforcing efficiency in the composites. \(E_f = 1050\) GPa [33], \(E_m = 1.2\) GPa, with 1 wt% MND weight concentration, \(V_f = 0.005\). For PVA/MND 1 wt% nanocomposites, \(E_c = 1.9\) GPa, \(\eta\) is, therefore, calculated to be 13.4%. For PVA/cMND 1 wt% nanocomposites, \(E_c = 2.4\) GPa, \(\eta\) is, therefore, calculated to be 23.0%. According to a simplified model by considering filler’s distribution, \(\eta\) is estimated to be 1/5 for 3D random distribution in the matrix and 3/8 for in plane random distribution. Therefore, the calculated \(\eta\) for PVA/cMND 1 wt% nanocomposites fit well with the theoretical value. Meanwhile, \(\eta\) of PVA/cMND nanocomposites increased by 71.6% compared to that of PVA/MND nanocomposites, which can be attributed to a good nanoparticle dispersion and better interfacial properties.

Table 3 shows the improvements on Young’s modulus (\(\Delta E\)), tensile strength (\(\Delta \sigma\)), onset temperature of thermal decomposition (\(\Delta T_{onset}\)), and thermal conductivity (\(\Delta \lambda\)) reported in the literature and this study.

| Samples                     | \(\Delta E\) | \(\Delta \sigma\) | \(\Delta T_{onset}\) | \(\Delta \lambda\) |
|-----------------------------|--------------|-------------------|----------------------|--------------------|
| Polyvinyl alcohol/DND (5 wt%) [22] | ~186%        | ~30%              | ~17 °C               | ~30%               |
| Cyanate ester/DND (2.5 wt%) [30] | ~8%          | ~19%              | /                    | ~28%               |
| Polydimethylsiloxane/DND (0.2 wt%) [34] | ~25%         | ~70%              | /                    | /                  |
| Polystyrene/DND (2 wt%) [35] | ~62%         | ~19%              | ~20 °C               | /                  |
| Nylon 6.6/DND (3 wt%) [36] | ~21%         | ~12%              | /                    | ~15%               |

In this study (3 wt%) | ~168%    | ~63%    | ~17 °C    | ~59%    |

\(\Delta E_c\), \(\Delta \sigma\), \(\Delta T_{onset}\), and \(\Delta \lambda\).
thermal stability and thermal conductivity compared with others. It is worth mentioning that these improvements were realized by one kind of cheapest nanodiamond precursor materials. However, we have to point out that, as mentioned earlier in TGA, the existence of water in PVA sample could cause a reduction in mechanical properties. Therefore, the values of Young’s modulus ($E$) and tensile strength ($\sigma$) are lower than the common values of PVA. The improvements on mechanical properties based on these relatively low values would appear greater than those in literature. Even so, we hope the above results of PVA/cMND nanocomposites can stimulate more researches on these MNDs in the future.

4. Conclusions

In this study, we utilized a designated low-temperature annealing and carboxylation process to obtain cMNDs with more oxygen-containing functional groups on their surfaces. Morphology, thermal and mechanical properties of pure PVA, PVA/MND, and PVA/cMND nanocomposites with different nanoparticle contents were investigated and discussed in detail. The cMNDs had a much better dispersion in PVA matrix even at as high as 10 wt% nanoparticle loadings compared with MNDs, due to the electrostatic interactions induced by oxygen-containing functional groups and thus formed hydrogen bonding with PVA molecules. Therefore, PVA/cMND nanocomposites achieved significant improvement on thermal and mechanical properties compared with pure PVA. For example, the glass transition temperature ($T_g$) and loss factor peak temperature ($T_{	an\alpha}$) of PVA/cMND nanocomposites were both shifted to higher values. The onset and maximum decomposition temperatures increased by over 17°C and 24°C, respectively. The thermal conductivity increased by 57.5% and showed a much higher value than the prediction model. Tensile strength and Young’s modulus of PVA/cMND nanocomposites increased by 62.3% and 166.7%, respectively, with 3 wt% cMND content. In summary, in terms of thermal and mechanical properties, the cMNDs with this designated low-temperature annealing and carboxylation process have higher reinforcing efficiency in polymer matrix than pristine MNDs and some cases of DNDs in the literature. Therefore, they are promising low cost and effective candidates for thermal and mechanical reinforcement for engineering polymer materials.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Notes on Contributors

Yuansai Zhang is a postgraduate student in College of Physics, Qingdao University.

Qingsong Hua is a professor in School of Mechanical and Electrical Engineering, and Dean of Power & Energy Storage System Research Center, Qingdao University. His research activities include functional materials, fuel cell power system etc.

Jian Min Zhang is a lecturer and researcher in College of Mechanical and Electrical Engineering, Power & Energy Storage System Research Center, Qingdao University.

Lili Zheng is a professor in National Institute for Materials Science, Japan. Her research activities include nanomaterials, functional materials for electrical applications.

ORCID

Jian Min Zhang http://orcid.org/0000-0003-2552-7485

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