EFFECT OF TYPE OF DIAMINE MODIFIERS OF NANODIAMOND ON TRIBO-MECHANICAL PROPERTIES OF POLYAMIDE 6 COMPOSITES

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ABSTRACT

In the present paper, two types of diamine components were used to investigate the effect of nanodiamond (ND) functionalization on mechanical and tribological properties of polyamide 6 (PA6) composites. Ethylene diamine (EDA) and hexamethylene diamine (HMD) were attached covalently onto the surface of NDs in a three-step wet chemical process. The optical microscopic (OM) images revealed that the dispersion state of ND-EDA particles is finer than ND-COOH and ND-HMD particles in PA6, due to high efficiency of EDA functionalization and less formation of agglomerates. Based on tensile testing, ND-EDA improved considerably young’s modulus and tensile strength of neat PA6 at 0.25 wt%. However, in the case of PA6/ND-HMD, improvement of mechanical properties was limited due to formation of ND-HMD agglomerates leading to stress concentrations in the composite. The friction and wear behaviour of PA6 composites were investigated under dry sliding condition using pin-on-disc tribometer. Incorporation of both diamine modified NDs enhanced the wear performance of polyamide 6. ND particles could serve as solid lubricants and improve the wear resistance. PA6/ND-HMD showed lowest coefficient of friction (COF) and lowest specific wear rate which can be attributed to easier transfer of ND-HMD particles from PA6 composite to wear zone leading to the formation of uniform and tenacious transfer layer.

1 INTRODUCTION

ND particle with diamond spherical structure has drawn great attentions due to its remarkable properties. Detonation process is an inexpensive method to produce ND on industrial scale [1,2]. High hardness and young’s modulus, chemical resistance, high electrical and heat conductivity and biocompatibility make ND particles suitable for many applications such as polymer composites. Nanosized and spherical shape of ND provides large surface to volume ratio which is an important feature for polymer composites [3–5].

Functionalization is one of the efficient ways to tailor the surface chemistry of ND and improve it for preparation of polymer nanocomposites. Surface of ND is covered by a graphitic shell consisting various functional groups such as carboxylic group, alcohol functions and ether groups. In the context of polymer composites, possible interactions between ND particles tend to formation of agglomerates. ND is completely flexible for further functionalization to improve the dispersion state and interactions between polymer and nanoparticles [4,6,7].

Detonated ND is mostly covered by oxygenated groups originated from its production method [7]. Researches were have tried to increase the concentration of carboxlated groups and improve the
purity of NDs. The literature shows thermal oxidization [8,9] and acid treatment [10–12] were employed for ND and CNT for this purpose.

Incorporation of functionalized carbon nanoparticles to different polymer matrix has been reported in literature [13–16]. Despite many advantageous of carbon nanoparticles, it is a controversial challenge to control the dispersion and distribution state of nanoparticles, especially in high viscosity mediums. In many cases, it is important to introduce a suitable surface modifier onto nanoparticle which is able to interact with surrounding polymer matrix in polymer nanocomposites.

Surface functionalization is also critical to obtain polymer/ND nanocomposites with improved performance. As an example of improvement of NDs interactions in polymer matrix, Haji ali and Shojaei [17] used silane functionalization to improve the compatibility between ND and polydimethylsiloxane (PDMS). According to their work, stable suspension of NDs was resulted in hydrophobic medium (PDMS) and the filler-polymer interfacial interactions were enhanced. It was assumed that functionalization of nanoparticles converts the particle-particle interaction to polymer-particle interaction. Hashemi and Shojaei [18] functionalized ND particles by introduction of hydroxy ethyl methacrylate (HEMA). Surface modified NDs were remained stable, distributed and spherical even at high shear rates of mixing of ND with unsaturated polyester resin showing the effectiveness of functionalization. Enhanced mechanical properties were also achieved even with one step thermal oxidization of nanoparticles [19]. Significant improvement of tensile modulus (~125%) and tensile strength (~85%) was achieved by adding carboxylated NDs (ND-COOH) at low concentrations (lower than 1.5 wt%) into chitosan. The authors attributed the high mechanical properties to development of thicker interphase with ND-COOH having higher degrees of carboxylic groups.

It is believed that ND filled polymer composites offer high wear resistant materials due to excellent tribological properties of ND. The improvement of wear performance is explained by ND diamond core structure, zero dimensional (spherical) shape, self-lubrication, reinforcement effect and size of agglomerates which lead to formation of tenacious transfer layer and wear resistant composites [20,21]. Although, most of the researchers were concentrated on thermoset resins [22,23], ND showed the potential for enhancement of wear properties of thermoplastic polymers [20].

In this work, tribological and mechanical properties of PA6 containing NDs with various diamine modifies. To this aim, ND particles were functionalized by two diamine modifiers through a wet chemical method. PA6/ND composites were prepared using melt mixing and then the samples were characterized.
2 EXPERIMENTAL DETAILS

2.1 Materials and Methods

ND was purchased from Nabond Tech China with average particle size of 4–6 nm, purity of 99%, density of 3.05–3.3 g cm$^{-3}$, specific surface area of 282 m$^{2}$ g$^{-1}$. PA6 (Akulon F223D) was obtained from DSM Co., The Netherlands. Ethylene diamine (EDA), hexamethylene diamine (HMD) thionyl chloride (SOCl$_2$), tetrahydrofuran (THF) and anhydrous ethanol were supplied by Merck and were all used as received.

Wet chemical surface modification of ND particles consists of three stages. As-received NDs was first oxidized in a furnace at 420 °C for 1.5 hr to increase carboxylate group content onto the nanoparticles. Then, the ND surface was activated using SOCl$_2$. ND-COOH particles were mixed with SOCl$_2$ and stirred for 24 hr at 65 °C to synthesize ND-Cl particles. The excess SOCl$_2$ were washed thoroughly with THF. These steps are similar for both surface modification methods.

In order to modify NDs with EDA, ND-Cl particles obtained in previous step were reacted with excess EDA at 60 °C for 24 hr. The solid powder (ND-EDA) was washed with THF to remove unreacted EDA. For the case of HMD, ND-Cl powder was reacted with excess HMD at 120 °C for 72 hr and then washed with anhydrous ethanol. Finally, ND-EDA and ND-HMD particles were dried in a vacuum oven at 40 °C overnight. Fig. 1 illustrates the sequence of surface modification of NDs with both diamine modifiers.

![Figure 1: Various steps of functionalization of ND with EDA and HMD.](image)

PA6/ND composites were prepared by an internal mixer (30/50 E, Brabender, Germany) and a counter-rotating twin-screw extruder (SHJ-20 Nanjing Giant, L/D=20). ND powder and PA6 granules were mixed using internal mixer at 220 °C and rotor speed of 80 rpm for 12 minutes. For further mixing and fabrication of composites at determined weight fraction (0.25 wt%), grinded granules obtained from internal mixer were diluted with neat PA6 by extruder. The temperature zones were set at 220, 225, 230 and 235 °C along the barrel and the rotor speed was 60 rpm. Three composite specimens are designated with abbreviations of PA6/ND-COOH, PA6/ND-EDA and PA6/ND-HMD. Here, ND-COOH is refered to carboxylated ND obtained from first step of surface modification procedure shown in Fig. 1.
2.2 Characterization

Dispersion state of NDs in PA6 matrix was investigated with transmission optical microscopy (TOM) using Olympus BX51m microscope. Tensile properties were measured by HIWA 2126 universal testing machine with a crosshead speed of 5 mm min\(^{-1}\) based on ASTM D638. Wear tests were conducted with a pin on disc tribometer, according to ASTM G99. The composite specimens were used as pins (5 mm diameter and 15 mm length) and counterpart disc was stainless steel. The wear tests were carried out at linear velocity of 0.26 m s\(^{-1}\), normal load of 80 N and 1500 m sliding distance. Neat PA6 and its composites were dried at 80 °C for 16 hr in a vacuum oven before all the tests to remove water absorption.

3 RESULTS AND DISCUSSION

3.1 Dispersion of NDs in PA6

TOM images of the nanocomposites are shown in Fig 2. The dark spots in the micrographs represent ND agglomerates in PA6. According to Fig. 2, PA6/ND-EDA has less and smaller agglomerates compared with PA6/ND-COOH which can be attributed to the surface modification of ND with EDA. However, PA6/ND-HMD image reveals poor dispersion state compared with ND-EDA and ND-COOH and more ND agglomerates.

Carboxylic groups containing polar oxygen that can make interactions like hydrogen bonds between ND-COOH particles. Steric hindrance arising from EDA modifiers inhibits the interactions between ND particles leading to less agglomerate formation [24,25].

Diamine functionalization of NDs with HMD is less efficient (based on FTIR spectra and TG analysis) than EDA. It can be concluded that fewer HMD components were attached covalently onto the surface of nanoparticles. Additionally, another possible explanation for bigger ND-HMD agglomerate is that longer hydrocarbon chain of HMD can bond two ND particles by its both amine groups. This intensifies the agglomeration and has an opposite effect on dispersion.

Fig. 3 depicts schematically the number and length of EDA and HMD modifiers on the surface of ND and also the agglomeration mechanism of ND-HMD particles. Therefore, dispersion state of NDs was affected by chemistry of the surface, effectiveness of modification and type of modifiers.

![Figure 2: TOM images of a) PA6/ND-COOH, b) PA6/ND-EDA and c) PA6/ND-HMD at 0.25wt%.](image)
3.2 Mechanical properties

Fig. 4 represents the stress-strain curves of neat PA6 and its composites. Tensile properties including elastic young’s modulus, tensile strength and elongation at break are listed in Table 1. As shown in Fig. 4, neat PA6 curve has a yield drop in comparison with PA6/ND-COOH and PA6/ND-HMD composites. This is due to interactions between the NDs particles and PA6 chains leading to reduction of mobility of polymer chains [26,27].

According to Table 1, elastic young’s modulus and tensile strength of PA6/ND-COOH were higher than neat PA6 showing the reinforcing effect of NDs in polymer matrix. Higher improvement of young’s modulus and tensile strength was achieved for PA6/ND-EDA. The tensile strength and young’s modulus were enhanced ~12% and ~27% respectively, for this composite. It is clear that improvement of tensile properties were dominated by dispersion of NDs in PA6.

Interestingly, PA6/ND-EDA also exhibited higher elongation at break with respect to ND-COOH and ND-HMD. Actually, presence of ND-EDA particles improved the toughness of PA6 through development of ND interphase with high mechanical properties [28].

Compared to PA6/ND-COOH and PA6/ND-EDA, incorporation of ND-HMD to PA6 has minor effect on mechanical properties enhancement. As discussed in previous section, ND-HMD particles has poor dispersion and more agglomerates. This leads to stress concentrations around the ND agglomerates and ineffective stress transfer from polymer matrix to reinforcement phase.
Table 1: Tensile properties of neat PA6 and composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PA6</td>
<td>2205 ± 109</td>
<td>62.3 ± 0.8</td>
<td>37.9 ± 5.2</td>
</tr>
<tr>
<td>PA6/ND-COOH</td>
<td>2576 ± 134</td>
<td>68.3 ± 1.0</td>
<td>22 ± 3.8</td>
</tr>
<tr>
<td>PA6/ND-EDA</td>
<td>2807 ± 156</td>
<td>69.5 ± 1.1</td>
<td>36.5 ± 4.9</td>
</tr>
<tr>
<td>PA6/ND-HMD</td>
<td>2250 ± 99</td>
<td>64.3 ± 1.1</td>
<td>16 ± 2.1</td>
</tr>
</tbody>
</table>
3.3 Tribological properties

Fig. 5 displays the variation of COF during the wear tests for PA6 composites. At the beginning of the tests, COF curves almost remain at a constant value. Then the COF values increases gently to reach the maximum value at approximately 1200 m.

Increasing the COF values was observed during the formation of transfer layer between counterpart surfaces. The transfer layer was loose at first since it was formed mostly by worn up PA6. With continuing the wear, ND particles were placed in wear zone and the transfer layer became tenacious. Finally, due to effective transfer layer and lubrication of NDs, COF curves reach to steady state zone with little increment, as seen frequently in literature [29,30].

Diamine functionalization of ND reduced the COF and specific wear rate of PA6 composites. Accordingly, specific wear rate of PA6/ND-EDA and PA6/ND-HMD is ~19% and ~27%, respectively, lower than PA6/ND-COOH. Improvement of PA6/ND-EDA is related to better mechanical properties which result wear resistant composite [31].

While the PA6/ND-HMD has the lowest mechanical properties among the PA6 composites, it showed lowest COF and specific wear rate. As shown in Fig. 2 (c), bigger agglomerates of ND-HMD were detected. It can be inferred that ND-HMD has less interactions with PA6 matrix. Therefore, ND-HMD agglomerates were drawn up easier at the same shear rate during the wear tests and effective transfer layer was formed sooner.
4 CONCLUSIONS

Thermal oxidization with subsequent EDA and HMD functionalization was performed to modify the ND surface. PA6 composites were prepared by melt mixing to use for tribo-mechanical characterization. Some conclusions can be drawn as follows:

- It was revealed that EDA functionalization improved the dispersion state (based on TOM images) through steric hindrance effect. Conversely, ND-HMD particles showed poor dispersion in PA6 which may be attributed to less effective functionalization or intensification of agglomerates formation.

- Tensile tests showed that the maximum increment in tensile strength (12%) and young’s modulus (27%) was achieved for PA6/ND-EDA composite. ND-EDA not only enhanced the stiffness of PA6, which is an indication of fine dispersion, but it improved the toughness of PA6.

- Improvement of wear properties, i.e. reduction of COF and specific wear rate, was closely related to surface modification and also formation of effective transfer layer.

REFERENCES


