Ultra-toughened nylon 12 nanocomposites reinforced with IF-WS₂

Fang Xu, Chunze Yan, Yat-Tarng Shyng, Hong Chang, Yongde Xia and Yanqiu Zhu

College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK
E-mail: y.zhu@exeter.ac.uk

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Abstract
Inorganic fullerene-like WS₂ nanoparticle- (IF-WS₂) reinforced nylon 12 nanocomposites have been prepared through effective ultrasonic mixing without using any surfactant, followed by molding at 220 °C. Morphological characterizations using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and microcomputed tomography (micro-CT) have revealed the excellent dispersion of IF-WS₂ nanoparticles in the nylon 12 matrix. X-ray diffraction (XRD) analyses have confirmed that a phase transition from α′-phase to a more stable γ-phase took place during the sintering of nylon 12, regardless of the amount of IF-WS₂ added to the matrix. At a very low IF-WS₂ content of 2 wt%, the tensile strength and bending strength of the composites increased slightly by 27% and 28%, respectively. However, the toughness dramatically improved by 185% and 148% at IF-WS₂ additions of 0.25 and 0.5 wt%, respectively, when compared to the neat nylon 12. It is believed that such improvements should mainly be attributed to the well-dispersed IF-WS₂ within the matrix. The vastly improved toughness suggests that the resulting polymer nanocomposites could be promising for structural and high-performance impact applications.

Keywords: nano composites, polymer-matrix composites, particle-reinforced composites, mechanical properties

(Some figures may appear in colour only in the online journal)

1. Introduction

In the past two decades, attention has been focused on improving the properties of traditional polymers by adding nanofillers. Notwithstanding the successful enhancement in stiffness, lower toughness and deteriorated ductility have been reported for most polymers reinforced with nanofillers. However, there are still several studies that reported improved toughness by incorporation of nanofillers into the polymer matrix [1–6]. In these studies, the improvement of toughness is normally attributed to different mechanisms, including interaction between particles and polymer matrix, crack deflection and local plastic deformation of the polymer surrounding the particles following debonding, the degree of mobility of the polymer chain, and the alteration of the crystalline structure and morphology of the polymer matrix resulting from the addition of nanoparticles [1–6]. Meanwhile, a better interface between the particles and the polymer matrix will improve thermomechanical properties, and significantly promote the thermal conductivity of nanocomposites [7].

Along with many interesting nanofillers, inorganic fullerene- (IF) structured WS₂ nanoparticles have recently attracted intense research interest due to their excellent solid state lubrication properties [8–12] and extraordinary shock-absorbing performance [13–15], owing to their hollow, close-caged, onion-like structures [12]. Furthermore, they are thermally stable and compatible with various systems. Incorporating IF-WS₂ into a proper matrix may lead to new composites with revised properties. Indeed, studies have shown that with low IF-WS₂ additions into a polymer matrix,
the composites exhibited improved thermal, rheological, and mechanical properties, compared to their neat polymers [16–20]. In an epoxy resin matrix, IF-WS2 simultaneously increased both the shear and peel strengths of the nanocomposites, as well as the toughness, which was attributed to a C-S bond formed between the IF-WS2 nanoparticles and the epoxy resin, as evidenced by the detection of an R-SO3 or R-SO3H band at 1246 cm⁻¹ in the FT-IR spectrum [16].

The purpose of this work was to utilize the superbly shock-absorbing IF-WS2 nanoparticles to reinforce nylon 12, an important engineering thermoplastic material widely used in industries, and to assess their influence on the thermal, morphological, and mechanical properties of the resulting nanocomposites.

2. Experimental setup

2.1. Preparation of nanocomposites

The nylon 12 (PA2200 Polyamide, melt flow index =1.86 ± 0.12) used in this study was supplied by EOS, Germany, as white powder. IF-WS2 nanoparticles with size ~50 nm and density of 3.9 g cm⁻³ were produced by a continuous reaction of WO3 (<100 nm, Sigma-Aldrich, UK) with H2S gas (BOC, UK) in Ar (BOC, UK) atmosphere, at 800 °C, in a newly designed rotary furnace, as previously described [21].

The as-produced IF-WS2 nanoparticles were first weighed and dispersed in ethanol for 1 h with the assistance of an ultrasonic probe, then mixed with the nylon 12 powder under intensive stir at 80 °C until all the ethanol vaporized. After being dried in an oven at 120 °C for 12 h, the well-mixed composite powders were then filled and pressed into a mold at 220 °C for 2 h to melt and produce the tensile and bending test samples, containing 0, 0.1, 0.25, 0.5, 2, and 4 wt% of IF-WS2.

2.2. Sample characterization

The mixed composite powders and compressed nanocomposites were appraised by x-ray diffraction (XRD) on a Bruker D8 Advanced x-ray diffractometer, with CuKα radiation (wavelength λ =0.154 nm), a step size of 0.02°, and a time step of two s for normal scan, over a 2θ range of 5–80°. A microcomputed tomography (micro-CT) scanner (Benchtop CT 160Xi, X-Tek) was used to analyze the porosity of the prepared nanocomposites. A JEOL JSM-6390LV scanning electron microscopy (SEM), operated at 20 keV, was used to visualize the morphology of both composite powders and nanocomposites. Both the powders and bulk samples were observed under back-scattered electron (BSE) mode, to avoid any coating required in secondary electron (SE) mode and to obtain correct energy-dispersive x-ray spectroscopy (EDX) information. Further transmission electron microscopy (TEM, JEOL 1400, operated at 120 kV) characterizations were carried out for the nanocomposites, to reveal the dispersion of IF-WS2 nanoparticles within the samples. The preparation of TEM specimens of the composite entailed several steps, including embedding into TAAB low-viscosity hard resin (TAAB Laboratories Equipment LTD); cutting out of the resin and gluing to a blank resin stub using Araldite epoxy resin; and microtome trimming and sectioning with a Diatome diamond knife into films that are approximately 100 nm thick, which were then floated onto Formvar-coated 300 mesh copper grids.

Raman spectra of the mixed composite powders and the bulk nanocomposites were acquired using a Renishaw RM1000 Raman microscope (RENISHAW, Wootton-Under-Edge, UK) with laser excitation at 532 nm and a 40x microscope objective lens. The thermal properties of produced samples were obtained using Q600-SDT equipment (TA instrument, USA). For each run, both thermogravimetric analysis (TGA) differential scanning calorimetry (DSC) curves were obtained from the results of approximately 20 mg of a dried sample, which was heated in an alumina crucible at a rate of 10 °C per min from room temperature to 1000°C under air atmosphere, in order to study the thermal stability against oxidation at elevated temperature.

Mechanical properties of the composites were evaluated using tensile and flexural testing. Tensile samples were finished and tested according to ASTM D638 standard, and three-point flexural testing was conducted in accordance with ISO178 [22], using a Lloyd Instrument EZZ0 on 10 and 1 kN load cells, respectively, at a loading speed of 2 mm min⁻¹. Three samples were tested for each type of composite.

3. Results and discussion

3.1. Dispersion of IF-WS2 nanoparticles in the nylon 12 matrix

Dispersion of nanoparticles is one major impediment to the development of high-performance polymer nanocomposites. The properties of polymer nanocomposites are highly dependent on how uniformly the nanoparticles are distributed within the matrix.

The SEM images of the composite particles containing 0.1 and 2 wt% of IF-WS2 are presented in figure 1. In the images, the bright WS2 nanoparticles are seen to locate separately on the nylon 12 particle surface, indicating very efficient powder mixing. The inset EDX spectrum in figure 1(a) confirms that the bright dots consist of W and S, attributed to IF-WS2 nanoparticles under BSE mode. For comparison, a denser distribution of the IF-WS2 is observed in figure 1(b) for samples with 2 wt% IF-WS2 loading. Accordingly, the EDX spectrum (figure 1(b), top left inset) shows higher signal intensities for the IF-WS2 particles investigated, which should be aggregates of IF-WS2 nanoparticles.

The distribution of WS2 in the bulk nylon 12/IF-WS2 nanocomposites is displayed in the TEM image in figure 2. IF-WS2 nanoparticles are represented by the dark dots in the matrix, which exhibits much lower contrast because of its low density. A very good dispersion of the 0.1 wt% IF-WS2 nanoparticles is shown in figure 2(a), with most of the
nanoparticles individually dispersed in the matrix, with the occasional two or three particles agglomerating together.

In figures 2(b) and (c), the 0.5 wt% of the IF-WS$_2$-loaded sample also showed a uniform nanoparticle distribution, with the majority of the nanoparticles isolated from each other. From these images, it can also be estimated that a higher amount of particles are impregnated within the matrix by comparing figures 2(a) and (c), which reflect the morphological differences between the additions of 0.5 wt% and 0.1 wt% IF-WS$_2$. When a much higher concentration of 2 wt% IF-WS$_2$ nanoparticles is impregnated into the nylon 12 matrix, the dispersion of IF-WS$_2$ still appears to be very good,
as shown in figure 2(d), although agglomerations of three or more particles occurred more often.

Micro-CT was applied to evaluate the porosity of the bulk composites, and the results are shown in figure 3. In each section view, very dense structures were observed, with the view from right displayed in figure 3(a); no voids were detected throughout the samples. This confirms the successful molding process. Furthermore, by varying the contrast during CT imaging, the polymer, which has a much lower density and exhibits much lower contrast than the IFs, could be tuned to become fully transparent, leaving only the IF-WS$_2$ nanoparticles visible. Although theoretically the size of the nanoparticles is undetectable with a normal micro-CT that has a resolution of 3 $\mu$m, it is believed that the extremely high density of WS$_2$ in fact sparked during scanning and, as a result, the particles near each other became visible, allowing the nanoparticle distribution in the composites to be clearly revealed. Based on this, the distribution of nanoparticles in composites with 0.1 and 0.25 wt% additions are shown in figures 3(b) and (c). As confirmed by the two-dimensional SEM/TEM analyses, the particles are indeed well-dispersed in a three-dimensional regime throughout the entire samples, based on micro-CT analyses. A much denser distribution of IF-WS$_2$ nanoparticles in the 0.25 wt% composite was also observed, compared with the 0.1 wt% sample.

3.2. XRD and crystalline structure

Several crystalline structures have been defined for nylon 12. It is well-accepted that the $\alpha$-phase and $\alpha'$-phase of nylon 12 are monoclinic; both show two characteristic diffraction peaks in XRD patterns at room temperature. Normally, the structure possessing two distinct diffraction peaks with a $d$ spacing of 0.37 and 0.44 nm is designated to $\alpha$-phase, while $\alpha'$-phase exhibits two crystalline peaks that are much closer to each other [23]. On the contrary, only one strong peak is presented in the $\gamma$-form, at a $d$ spacing of about 0.42 nm [23, 24].

The XRD profiles of both powdered composite samples before sintering and bulk composite samples after sintering
are shown in figures 4(A) and (B), respectively. As a semi-crystalline polymer, two strong peaks of pure nylon powder are presented at $\Theta = 21.08^\circ$ and $\Theta = 22.08^\circ$, respectively (profile a in figure 4(A)), corresponding to $d = 0.421$ nm and $d = 0.402$ nm of the $\alpha'$-phase of nylon 12, which is believed to be a less stable phase [24]. However, only one distinct peak appears at $\Theta = 21.42^\circ$ ($d = 0.415$ nm) for the bulk nylon sample after sintering (profile a in figure 4(B)), which is attributed to a more stable $\gamma$-phase at room temperature [24, 25]. This is in good agreement with previous studies, where annealing and sintering processes from the melt at atmospheric pressure lead to the formation of $\gamma$-phase [26]; a similar phase transition from $\alpha'$-phase to $\gamma$-phase has been observed on cooling from crystallization temperature to room temperature in another study [23].

Due to the low content of IF-WS2 in the composites, only the peak at $\Theta = 14.3^\circ$ and a broad peak, presumably a combination of 32.7° and 33.6°, appeared in the XRD patterns, which should be assigned to IF-WS2 (JCPDS No. 84-1398). These peak intensities increase gradually with the amount of content in both the powder and bulk composites, from a very tiny signal for 0.1 wt% to a vivid peak for 0.5 wt%, to a distinct peak in 2 and 4 wt%, as expected. Furthermore, it is noted that, regardless of the IF-WS2 content, the composite samples exhibited identical signals associated with the nylon 12, and the two peaks at 21.08° and 22.08° belonging to the $\alpha'$-phase for the powder, and only one major peak at 21.4° for the bulk, suggest that a $\gamma$-phase was always observed. It is also noteworthy that the relative intensity ratio for the peak at 21.4° for the (001) plane, to other peaks of $\gamma$-phased nylon 12 (e.g., the peak at around 27.5°), has increased for 0.1 wt%, 0.25 wt%, and 0.5 wt% IF-WS2 samples. However, it decreased for 2 and 4 wt% samples (which is even lower than that of pure nylon). This intensity change is believed to result from the $\gamma$-phase content change in the matrix, and will have an effect on the mechanical performance, especially the strain, of composites, since the $\gamma$-phase crystal is believed to be ductile and will benefit the toughness of the composite [6].

3.3. Raman

Figure 5(A) displays the Raman spectra of a series of powder composites before sintering. Peaks at 350 cm$^{-1}$ and 419 cm$^{-1}$ should be assigned to the $E_g$ and $A_{1g}$ modes of IF-WS2 [27], both starting to appear from spectrum b, with the intensities becoming more and more dominant in spectra c and f, as highlighted in the top left inset. All the other peaks are assigned to nylon 12. Compared with previous studies [28–30], the majority of Raman shifts for nylon 12 are detected, as shown in figure 5(A). Shifts at 2924 cm$^{-1}$ and 2800–2900 cm$^{-1}$ (2839 cm$^{-1}$ and 2874 cm$^{-1}$) are assigned to the CH$_2$ asymmetric and symmetric stretching, respectively. The amide I peak appears at 1632 cm$^{-1}$. Shifts located at 1434 cm$^{-1}$, 1364 cm$^{-1}$, and 1293 cm$^{-1}$ are attributed to the bending, wagging, and twisting of CH$_2$, respectively [31]. The shift for amide III occurs at 1266 cm$^{-1}$. The NH wagging has resulted in two peaks at 1219 cm$^{-1}$ and 1244 cm$^{-1}$. There are several primary peaks at around 950–1200 cm$^{-1}$, which should be assigned to the CH$_2$ stretching mode, while the C-CO stretching accounts for shifts at 910 cm$^{-1}$ and 937 cm$^{-1}$. CH$_2$ rocking might result in the peak at 715 cm$^{-1}$. The shift appearing at 633 cm$^{-1}$ should be defined to Amide IV (d CO) [29] and the characteristic peak for N-H out-of-plane bending is presented at 611 cm$^{-1}$ [31].

Figure 5(B) shows the Raman spectra of the bulk nylon 12/IF-WS2 composites in powder form before sintering (A) and in bulk form after sintering (B), with different amounts of IF-WS2 content: (a) 0 wt% IF-WS2; (b) 0.1 wt% IF-WS2; (c) 0.25 wt% IF-WS2; (d) 0.5 wt% IF-WS2; (e) 2 wt% IF-WS2; and (f) 4 wt% IF-WS2.
4 wt% IF-WS2, respectively (figure 5(B)). Furthermore, the peak at 633 cm$^{-1}$ in bulk composites is not as sharp as that of the powder sample, regardless of the IF-WS2 content.

3.4. DSC and crystallization

The DSC curves displayed in figure 6 showed that all samples exhibited a melting peak at around 180 °C (figure 6(A)), an initial exothermic peak at around 350 °C, and a final broad exothermic peak after 500 °C (figure 6(B)). However, the main exothermic peaks between 400–500 °C are very complicated, with a feature of multiple peaks for all the samples. This is possibly due to the stochastic chain deformation and decomposition of nylon 12 during the oxidation process, especially since the oxidation of WS2 might involve the formation of sulphides, which make the peaks more complex [32].

3.5. TGA and thermal stability

For as-produced IF-WS2 nanoparticles, the oxidation in air starts from 350 °C [21], while for nanocomposites little change in their onset thermal stability was observed, as verified by the TGA results displayed in figure 7. Below 450 °C, the 0.1 wt% and 0.25 wt% IF-WS2 composites exhibit higher oxidation temperatures than that of the pure nylon 12, and the 0.5 wt% composites only display a marginally better performance against the neat matrix. When the IF-WS2 contents were increased to 2 and 4 wt%, the composites exhibited a poorer thermal resistant behaviour compared to the pure nylon 12. At 450 °C and higher, the weight loss of 2 wt% and 4 wt% composites became less than other composites, probably due to the formation of carbidies, oxides, and sulphides following oxidation of IF-WS2, thus resulting in a delayed weight loss when compared to other samples from 450–550 °C. Above 550 °C, because of the higher amounts of residue weight of tungsten oxide to the oxidation of IF-WS2, there is a good correspondence between the residual weight and the WS2 content of the sample.

3.6. Mechanical properties

Typical stress-strain curves are displayed in figure 8(A), which shows the significantly improved strength and ductility of the composites, compared to neat nylon 12. From 0.1 up to 2 wt%, an improvement of 27% in tensile strength is shown for the 2 wt% composite; a slight decrease is shown for the 4 wt% samples, compared to the neat nylon 12, as seen in figure 8(B). The Young’s modulus, as defined by the slope of the initial liner part of the stress-strain curve, also increased with higher IF-WS2 content until 2 wt%; it then decreased for the 4 wt% samples. Similarly, the strains first increased, and then decreased dramatically after 2 wt%. The 4 wt% samples became brittle, with a strain as low as 13.2%, and they broke before the yielding point, as seen in figure 8(A). Obvious necking behaviour was observed for samples of 0 to 2 wt% IF-WS2 content. It is noted that there is a significant increase in elongation at break for the composites with low IF-WS2 content.
additions of up to 0.5 wt%, indicating remarkably improved ductility, as shown in figure 8(D). However the elongation at break started to decrease for the 2 wt% samples, compared to neat nylon 12, and became brittle for the 4 wt% samples, which displayed a sharp fracture surface without any necking behaviour. This could be related to the \(\gamma\)-phase content change in the nylon 12 samples, as discussed above and revealed by the XRD intensity of (001) peak for nylon 12. In addition, the changes in ductility could also be ascribed to the dispersion of IF-WS\(_2\) nanoparticles in the polymer. With higher amounts of nanoparticles, the dispersion of IF-WS\(_2\) became more difficult. The agglomeration would impede deformation and result in local stress concentration, thus leading to a decrease in elongation at break. This will be addressed further in the discussion for toughness.

Three-point flexural tests were also carried out for the composite samples, and the average bending strengths are displayed in figure 8(C). Except for the 4 wt% IF-WS\(_2\) samples, which broke during the bending tests, all other samples survived after a 22 mm deflection and exhibited very good plastic characteristics. An increment in bending strength was clearly shown with increased IF-WS\(_2\) content, from 67.2 MPa for neat nylon 12 to 85.6 MPa for the 2 wt% IF-WS\(_2\) samples. However, a decrease then followed, which means the composites became brittle at 4 wt%, and the specimens broke at an average deflection of 13 mm, with a final bending strength of 79 MPa. Mechanical data for nylon 12/IF-WS\(_2\) composites were summarized in table 1.

Normally, elongation at break (in other words, ductility) is a requisite for toughness. A tough material must possess high ductile performance. However, a material with high ductility would not necessarily be a tough material without high stiffness. Defined as the ability of a material to absorb energy before fracture, toughness of materials could be evaluated by several approaches. In this study, the area under the stress-strain curve was used to demonstrate the toughness of the IF-WS\(_2\)/nylon 12 composites (figure 8(E)). An increase was observed for nanocomposites with 0.25 wt% and 0.5 wt% IF-WS\(_2\), which is 285% and 248% of that of neat nylon 12, respectively. As discussed above, toughness is a combination of strength and ductility, so the 2 wt% samples showing a lower toughness value than that of the neat nylon 12 is not surprising, although they have much higher tensile strength. For the same reason as for changes in ductility, the decrease of toughness could be attributed to the \(\gamma\)-phase content in the nylon 12 composite samples, which is higher in low content samples and lower in the 2 and 4 wt% samples, as compared to neat nylon 12 sample (figure 4(B)).
also be worked out from the bending stress-strain curve, and a toughness modulus of 5.20 MJ m$^{-3}$ for the 4 wt% samples is obtained, which is in excellent agreement with that obtained from its tensile behaviour (5.21 MJ m$^{-3}$).

The tensile fractured surfaces of the composites are shown in figure 9. Both the 0.5 wt% (figures 9(a) and (b)) and 2 wt% (figures 9(c) and (d)) samples showed a well-dispersed IF-WS$_2$ nanoparticle within the matrix, while the distributions within the 2 wt% samples are much thicker than that of the 0.5 wt% specimens. A higher volume of IF-WS$_2$ in the polymer would encounter severe agglomeration, which causes local stress concentration, resulting in lower toughness.

Although the IF-WS$_2$ nanoparticles themselves could act as an excellent shock absorber [13, 14], such influence in present composites would be minimal, due to the low fraction added and the slow loading speed applied.

**Figure 9.** BSE mode SEM images of the fracture surface of the IF-WS$_2$ nylon 12 composites ((a) and (b): 0.5 wt%; (c) and (d): 2 wt%), showing the role of the embedded particles in the matrix while breaking.

**Table 1.** A comparison of the mechanical properties of nylon 12/IF-WS$_2$ composites.

| IF-WS$_2$ content (%) | Tensile stress (MPa) | Young’s modulus$^a$ (MPa) | Toughness$^a$ (MJ m$^{-3}$) | Elongation at break$^a$ (%) | Bending stress (MPa) |
|-----------------------|---------------------|--------------------------|-----------------------------|---------------------------|-------------------|
| 0                     | 48.7                | 780                      | 14.86                       | 37                        | 67.1              |
| 0.1                   | 52.9                | 937                      | 21.44                       | 48                        | 72.2              |
| 0.25                  | 54.5                | 968                      | 42.42                       | 97                        | 78.9              |
| 0.5                   | 55.9                | 997                      | 36.80                       | 79.8                      | 79.9              |
| 2                     | 61.5                | 1176                     | 12.56                       | 24.7                      | 85.6              |
| 4                     | 52.4                | 874                      | 5.21                        | 13.2                      | 79                |

$^a$ Young’s modulus, toughness and elongation at break data are based on the tensile tests.
These results show that the resulting nylon 12/IF-WS$_2$ composites are of high quality with regard to their mechanical properties against the neat nylon 12, which also exhibited a higher tensile strength compared with reports in the existing literature [33, 34]. This may be partly due to the relatively high density obtained at present (i.e., no voids, as confirmed by the micro-CT analyses, as seen in figure 3). The polymorphism could be another reason, from the presence of $\gamma$-phase evidenced by the XRD results. The main reason is believed to arise from the large areas of interface between the IF-WS$_2$ nanoparticles and the nylon 12 matrix. Under loading, the well-dispersed IF-WS$_2$ nanoparticles would promote load transfer efficiency, helping to stop or delay defect propagation, thus leading to improved strength.

4. Conclusions

An efficient fabrication process has been applied to prepare IF-WS$_2$-reinforced nylon 12 nanocomposites. Combined characterizations have revealed the excellent dispersion of IF-WS$_2$ nanoparticles at low fractions. The nylon 12 matrix exhibited a $\alpha'$-phase to a more stable $\gamma$-phase transition during the sintering process, regardless of the amounts of IF-WS$_2$ added. The composites showed a marginal improvement in thermal stability, and moderate improvements in tensile strength and bending strength, by 27% and 28%, respectively, for 2 wt% IF-WS$_2$ composites. They also showed significant improvements in toughness, by 185% and 148% with 0.25 and 0.5 wt% of IF-WS$_2$ added, respectively, benchmarked against the neat nylon 12. The mechanical property improvements should be attributed to the well-dispersed nanoparticles in the polymer matrix.

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