

Effect of phosphoric acid on the morphology and tensile properties of halloysite-polyurethane composites



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ABSTRACT

The high aspect ratio of nanoscale reinforcements enhances the tensile properties of pure polymer matrix. The composites were first made by adding halloysite nanotubes (HNTs) at low weight percentages of 1, 2, and 3 wt% to thermoplastic polyurethane (TPU). Then, HNTs were phosphoric acid-treated before adding to TPU at same weight percentage to create phosphoric acid HNTs-TPU composites. The samples were fabricated using injection moulding. The HNTs-TPU composites were characterized according to the tensile properties including tensile strength, tensile strain and Young's modulus. The loading has shown its highest tensile values at 2 wt% HNTs loading and same findings are shown with the samples that treated with phosphoric acid. The tensile strength increased to reach 24.65 MPa compare with the 17.7 MPa of the neat TPU showing about 26% improvement. For the phosphoric acid-treated composites, the improvement has reached 35% compared to the neat sample. Regarding the tensile stain, the improvement was about 83% at 2 wt% HNTs loading. For Young's modulus, the results obtained in this study have shown that Young's modulus is linearly improved with either the loading content or the phosphoric acid treated achieving its highest values at 3 wt% HNTs of 14.53 MPa and 16.27 MPa for untreated and treated, respectively. FESEM results showed that HNTs were well dispersed in TPU matrix. Thus, HNTs-TPU has improved tensile properties compared with pure TPU due to the addition of nanofiller.

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Introduction

In addition to TPU, HNTs, whose structure is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, have become a very important mined natural product in nanotechnology [1–4]. HNTs, treated or untreated with acids, are additive products at very low ratios to TPU to create composite who's physical and chemical properties may drastically improve. Nanotechnology has evolved in the last three decades and since then numerous areas of production were benefited with new and more reliable products as in the medical fields [5–7] and in the production of high-quality porcelain [8]. The HNTs are nanoadditive that has been used to enhanced the mechanical [9], thermal, crystallization, and fire performance of thermoplastic polymers (e.g., polypropylene and polyamide-6) [10]. HNTs was found to be a viable and inexpensive nanoscale container for encapsulation of drugs that was first demonstrated by several researchers [11,12]. The use of HNTs has shown better outcome compared with

the traditional nanofillers of carbon nanotubes (CNTs) due to cost and easy processability [2]. Nanotubes such as HNTs or carbon nanotubes (CNTs) are very effective with even small quantities of loading with polymers such as thermoplastic nanoparticles, which could result in significant changes in the physical and chemical properties [13].

Injection is not a new technology; it is a rather very old technique that had used for many centuries at a very low creativity. Recently, injection moulding has become one of the fastest technique due to its importance in many fields such as automotive, screens, and films [14]. In plastic processing technology, in particular, injection is considered as the top technique due to automation, precision, material utilization, and good flexibility to complex geometry [15]. TPU, as one of the most used plastic, has been employed extensively due to its excellent physical properties such as low flexibility, high tensile strength, and abrasion resistance, solvent resistance, and high versatility in chemical structure [16]. The main world's polyurethane market is used for the applications of coatings, adhesives, sealants, and elastomers [17,18]. TPU can be an improving factor in many services such as thermal

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stability, and mechanical properties where TPU plays an important role in chemical properties [19].

This article discusses the effect of two parameters, namely, the effect of the percentage additive ratio and how phosphoric acid plays an important role in the process of tensile properties enhancement.

Experimental

Materials

HNTs, in powder form with an average size of 20 nm, were purchased from Natural Nano, Inc., 832 Emerson Street, Rochester, New York. TPU semi-round-Ester type of about 5 mm in diameter was purchased from Global Innovations-polycarbonates Bayer Material Science AG, D-51,368 Leverkusen.

Preparation of composites

HNTs and TPU were dried in an oven at 80 °C for 12 h to reduce the amount of absorbed water due to storage effect [20]. The first patch of three samples was prepared by mixing 0.5, 1.0, and 1.5 g HNTs with 49.5 g, 49.0 g, and 48.5 g TPU, respectively using Brabender mixer at mixing temperature (200 °C), screw speed (30 rpm), and mixing time (40 min) [21]. The three samples of the first patch were labelled with 1, 2, 3 wt% untreated HNTs-TPU composites. The other three samples are prepared by using treated HNT's with phosphoric acid. The procedure of creating these three samples started by dissolving 15 g HNTs in 100 ml 3M-phosphoric acid at 90 °C rate and mixed at a rate of 200 rpm for 8 h [22] followed by drying procedure. The second patch was prepared by taking same ratios as in the first patch with treated HNTs. The three samples were labelled with 1, 2, and 3 wt% acid treated HNTs-TPU composites.

Testing equipment

The mixture of the composites was performed with a Brabender mixer (Model W 50 EHT) Corder PL 2000 compounder equipped with a 50 cm³ kneader chamber. For the preparation of specimens for testing, the injection apparatus DSM Xplore moulding injection machine was used. The chamber of 10 cm³ can be heated up to 350 °C. Tensile properties were experimentally measured using an Instron 5567 machine, according to ASTM D-638 type V [14]. Three specimens were tested with a crosshead speed of 50 mm/min [14]. FESEM, model ZEISS SUPRA 55-VP (Manufacturer, Konigsallee, Deutschland) with a magnification up to 25.00 kx, was used to investigate and view small structures on the surface of the HNTs-TPU composites. FTIR analysis is performed using a Perkin

Elmer System 2000 (Waltham, MA, USA), which is equipped with attenuated total reflectance. For this research, FTIR of resolution 4 cm⁻¹ was run between 400 and 4000 cm⁻¹.

Results and discussion

Morphology of HNTs

Fig. 1 shows the FESEM images of HNTs before and after sulphuric acid treatment. The focus in these Figure is about the distribution of the nanotubes before and after sulphuric acid treatment. Considering the nature of FESEM images which signifies the distribution of the nanotubes with the virtually unlimited depth of field in the matrix rather than horizontally on the surface, the images did not clearly show the exfoliation of the outer surfaces. The stacking of HNTs clearly shows the effect of sulphuric acid on the distribution of HNTs. As the acid treatment, the HNTs became separable HNTs treatment where the HNTs appeared very mixed with no distinguishable physical feature of the nanotubes themselves.

Morphology of TPU

The fractured surface of the TPU matrix is shown in Fig. 2(a). The surface does not show irregularities and seemingly TPU still behaves as a bulk material. When TPU is enforced by 1 and 3 wt% untreated HNTs, the images of the fractured surfaces show the presence of untreated HNTs distributed in the matrix as depicted in Fig. 2(b and c). The amount of untreated HNTs on the fractured surface of 3 wt% untreated HNTs-TPU composites is clearly about three times that on the surface of 1 wt% untreated HNTs-TPU composites as shown in Fig. 2(b and c), respectively. A close investigation of Fig. 2(b and c) reveals that surface morphology improved for 3 wt% untreated HNTs-TPU as the cavities are much less in both the size and number. For the 3 wt% untreated HNTs-TPU composites, the surface looks smoother than that of 1 wt% untreated HNTs-TPU composites. The cavities shown on the fractured surface of the TPU matrix disappeared or their sizes were reduced significantly. Disappearing of cavities suggests that the tensile strength becomes better than that of neat TPU. The second modification for HNTs-TPU composites was conducted by treating HNTs with acid treated HNTs at 1, 2, and 3 wt% to create three samples of untreated HNTs-TPU composites as explained earlier. FESEM images of 1 wt% acid treated HNTs-TPU composites and 3 wt% acid treated HNTs-TPU composites are shown in Fig. 2(d and e). The fractured surface becomes very smooth as the acid treated HNTs distribution becomes very clear. When acid treated HNTs reached 3 wt%, the composites surface becomes distinctive and a good amount of acid treatment HNTs are broken which, possibly, reflects on the characteristics of the composites.

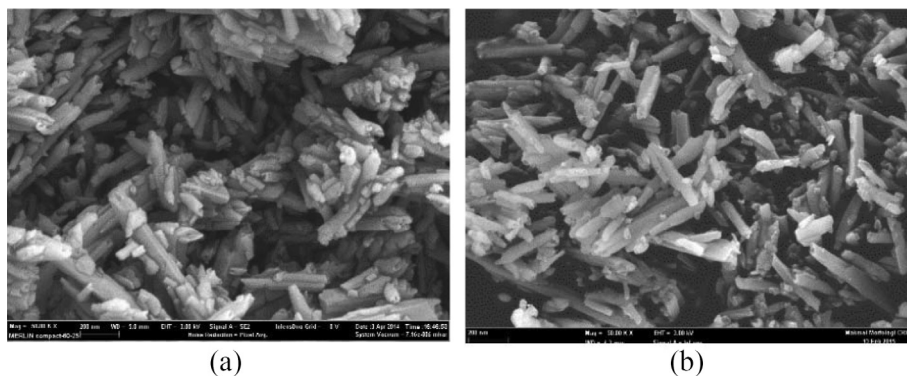


Fig. 1. FESEM microphotographs of (a) Neat HNTs and (b) Phosphoric acid treated of HNTs.

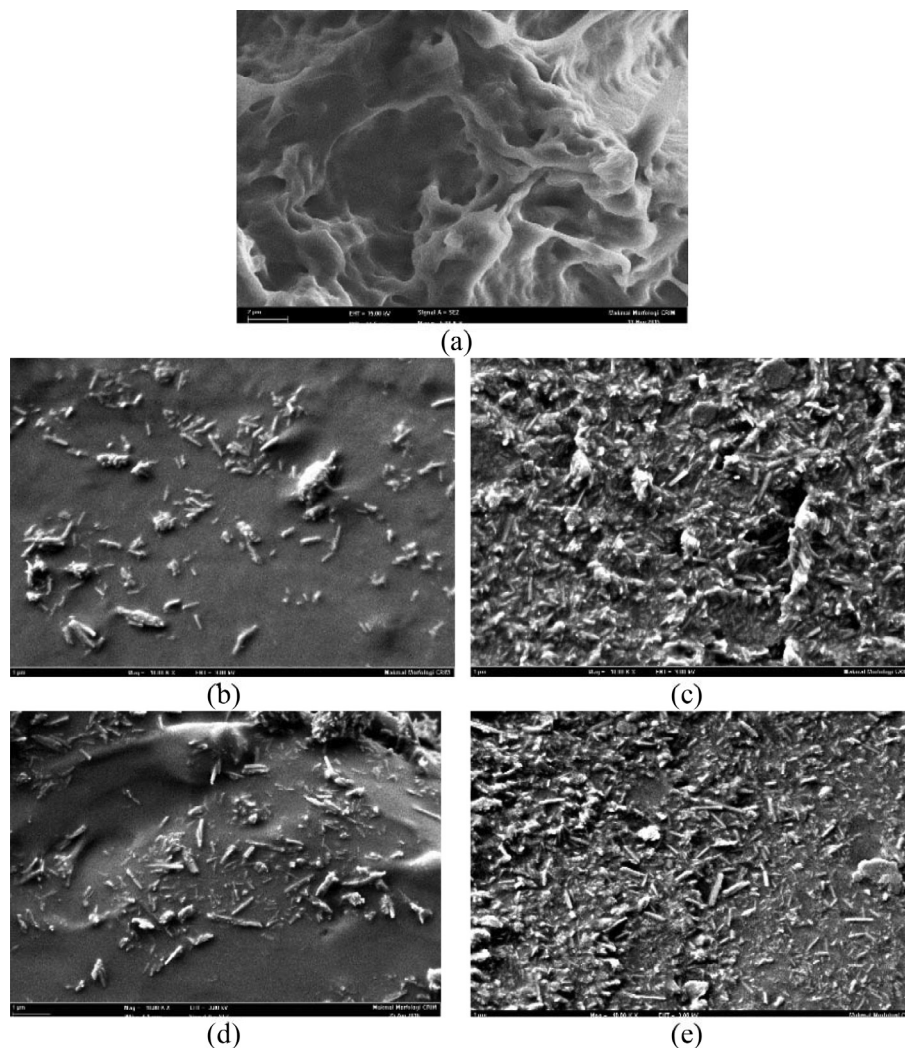


Fig. 2. FESEM (10 kx) of (a) TPU matrix, (b) 1 wt% untreated HNTs-TPU composites, (c) 3 wt% untreated HNTs-TPU composites, (d) 1 wt% acid treated HNTs-TPU composites, (e) 3 wt% acid treated HNTs-TPU composites.

Table 1
Tensile properties of HNTs-TPU composites.

Sample	Tensile strength MPa	Tensile strain %	Young's modulus MPa
Neat TPU	17.7	430.3	2.3
1 wt% untreated HNTs-TPU	20.78	569.1	9.22
2 wt% untreated HNTs-TPU	23.34	832.6	12.65
3 wt% untreated HNTs-TPU	19.44	577.2	14.53
1 wt% acid treated HNTs-TPU	21.81	671.9	11.25
2 wt% acid treated HNTs-TPU	24.65	854.7	14.32
3 wt% acid treated HNTs-TPU	20.85	745.7	16.27

Influence of HNTs loading on the tensile properties of composite

The tensile properties under investigation include the tensile strength, tensile strain, and Young's modulus. Each composition was made at three samples and each sample was experimentally treated. The averaged results of the tensile strength, tensile strain, and Young's modulus of the seven samples are listed in Table 1. The highest values of the tensile strength were obtained at 2 wt% untreated HNTs-TPU composites and 2 wt% phosphoric acid treated HNTs-TPU composites at 23.34 MPa and 24.65 MPa, respectively. The results suggest that the improvement in the tensile

strength were 26% and 35% for the two samples, respectively. The improvement of both samples can be attributed to the additive HNTs while for the acid-treated sample, the improvement was attributed to both HNTs and the better dispersion of HNTs in the bulk. The dispersion occurred between the layered silicate of HNTs and the TPU chains [19].

The results of tensile strength, tensile strain, and Young's modulus for neat TPU sample, untreated HNTs, and acid-treated HNTs composites in Table 1 are documented in Fig. 3(a)–(c), respectively. As shown in Fig. 3(a), the highest treated of 3 wt%, the tensile strength of the untreated and treated declined compared to the 2 wt% samples from 23.34 to 19.44 MPa and from 24.65 to 20.85 MPa, respectively. At higher loading above 3 wt% HNTs-TPU composites, the tensile strength decreases which could be attributed to the agglomeration of the HNTs which naturally leads to poor interaction between HNTs and TPU. Similarly, the tensile strength, the tensile strain of untreated and treated has its highest values at 2 wt% samples has shown improvement by 725.8% and 788.9%, respectively as shown in Fig. 3(b). These results show that the tensile strain has improved by about 10% which is very close to the improvement of the tensile strength. The Young's modulus results shown in Table 1 for the same sequence are shown in Fig. 3(c). Firstly, the results show that Young's modulus of the untreated samples increases linearly with wt% HNTs loading achieving the

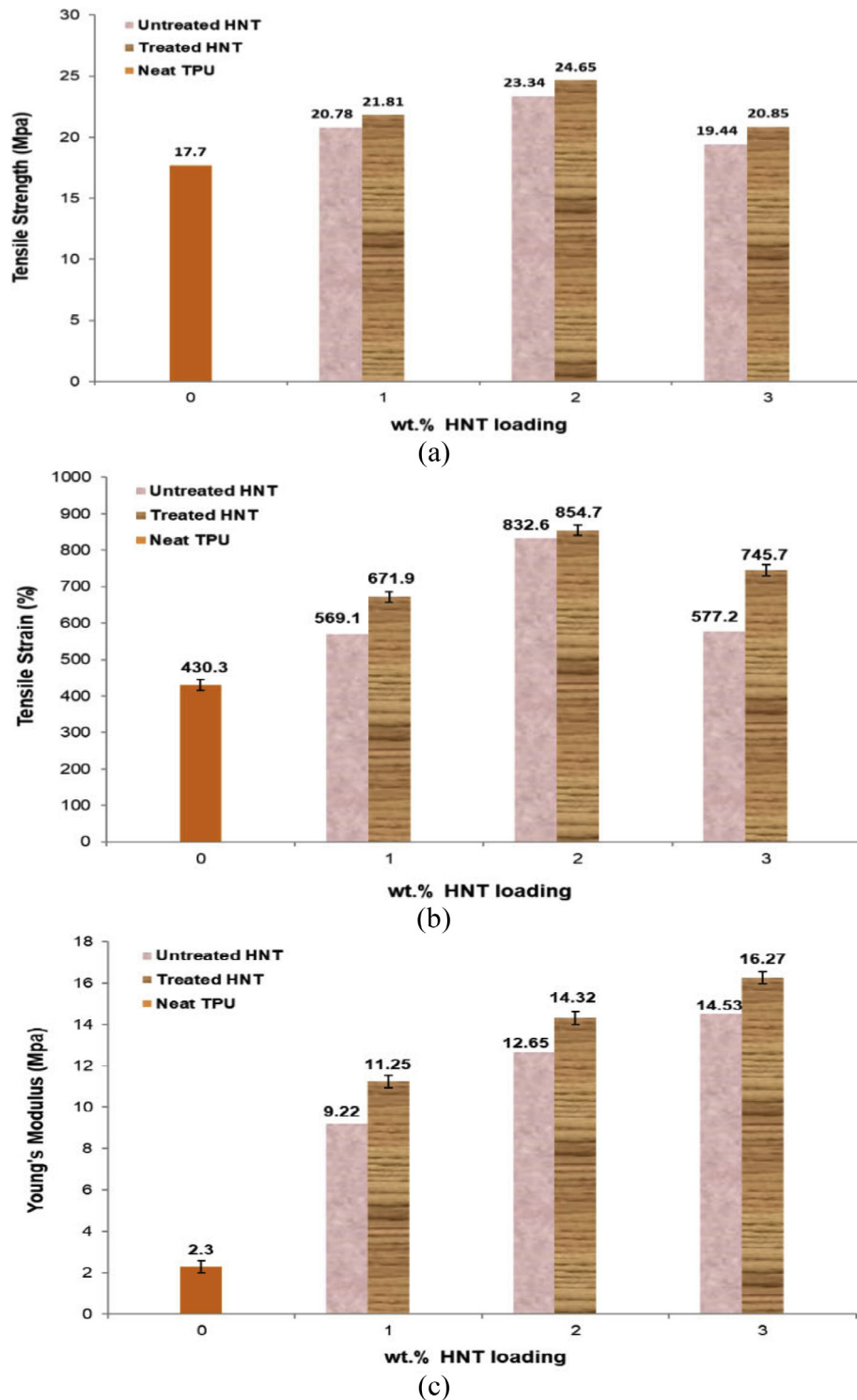


Fig. 3. Effect acid treated HNTs on the tensile properties of HNTs-TPU composites (a) Tensile strength, (b) Tensile strain and (c) Young's modulus.

highest Young's modulus at 14.53 MPa while Young's modulus of the treated samples was recorded at 16.27 MPa at the 3 wt% acid treated HNTs-TPU loading. Secondly, Young's modulus of 2 wt% acid treated HNTs-TPU composites and 3 wt% untreated HNTs-TPU composites do not show any difference.

Fourier transform infrared spectroscopy (FTIR)

Based on the results shown in Fig. 4(a), the FTIR spectrum of the HNTs asserts the following notes: the band at 3695.3 cm^{-1}

represents to the stretching vibration of the inner surface OH groups, while the band at 3624.3 cm^{-1} represents to the stretching band of the inner groups. The inner surface OH groups are connected to the Al-centered octahedral sheets and form hydrogen bonds with the oxygen sheet in the next double layer. Typically of halloysite, the other two inner surface OH groups that occur at approximately 3650 cm^{-1} and 3670 cm^{-1} cannot be observed. However, absorption bands observed 2356.6 cm^{-1} are due to the stretching of C-H bonds [23]. Absorption bands recorded at 1650.5 cm^{-1} , respectively, show very weak peaks that could not

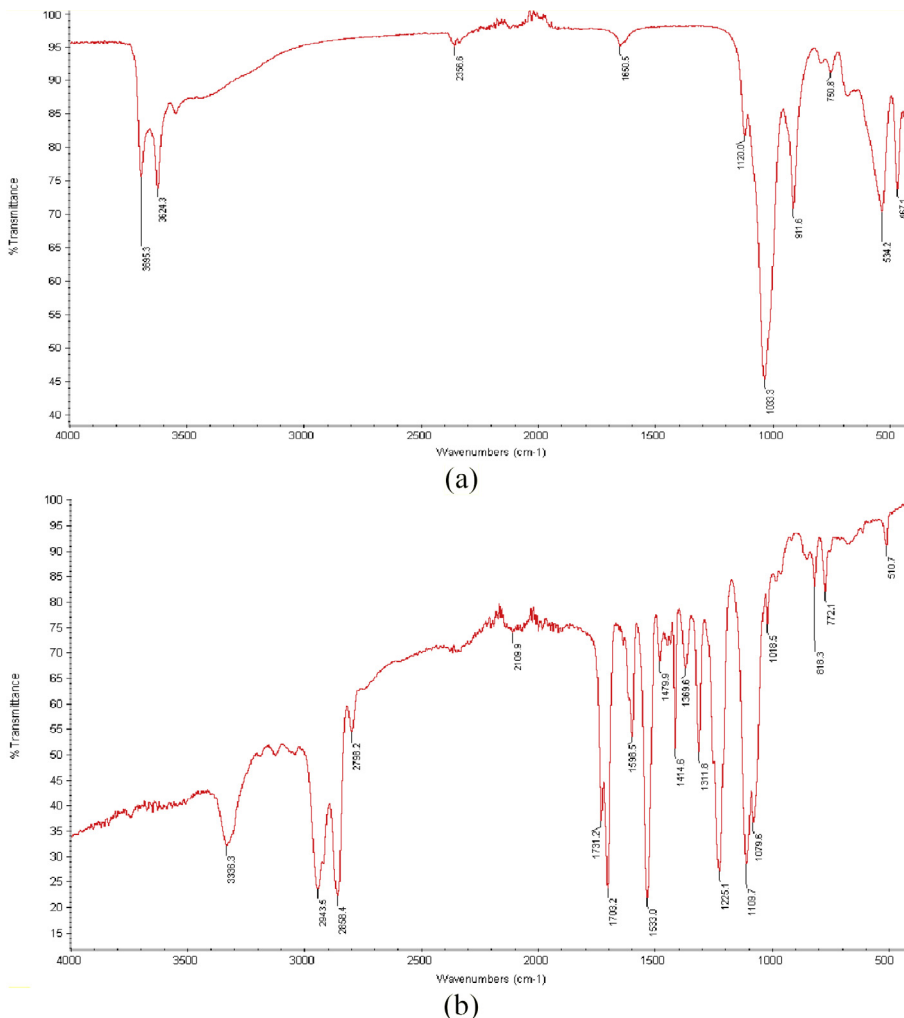


Fig. 4. (a) FTIR analysis of the HNTs. (b) FTIR analysis of the HNTs-TPU.

Table 2
FTIR assignments [25].

Bands Origin	Wavenumber (cm ⁻¹)	Assignment
N—H O—H	3336.3	Hydrogen bonded N—H vibration band and O—H
—CH ₂	2943.5	Methylene stretching vibration modes (asym)
—CH ₂	2858.4	Methylene stretching vibration modes(sym.)
	2798.2	Methylene stretching vibration modes(sym.)
	2109.9	Methylene stretching vibration modes(sym.)
C=O	1731.2	Hydrogen bonded urethane stretching vibration band
	1703.2	Free urethane stretching vibration band
—CH ₂	1596.5–1533	Methylene groups asymmetric bend vibration modes
	1479.9–1414.6	Methylene groups asymmetric bend vibration modes
C—N	1369.6–1311.9	C—N stretching vibration modes
	1225.1	C—N stretching vibration modes
C—O—C	1109.7	Ether stretching vibration (crystalline)
	1079.6	Ether stretching vibration
Si—O	1018.5	Stretching vibration mod
Si—O	818.3	Bending vibration mode
	772.1	Bending vibration mode
	510.7	Bending vibration mode

be reliably assigned to any possible bonds and might be due to impurities [22]. The bands at 1120.0 and 1033.3 cm^{-1} belong to Si–OH groups [22,24]. FTIR spectra of pristine HNTs-TPU composites are shown in Fig. 4(b). These typical bands are described in Table 2 and marked in Fig. 4(b) [25].

Conclusion

HNTs-TPU composites of high strength and modulus were prepared. The increased demands for light and strong materials was resonating with the invention of very strong and light composites materials. This work goes along that line by creating HNTs-TPU composites where a 26%-improvement was achieved in tensile strength compared to the neat TPU. Moreover, when HNTs are treated with phosphoric acid, the tensile strength was improved by 35% compared to the neat TPU for 2 wt% HNTs-TPU nanocomposite. Seemingly, phosphoric acid resulted in better characteristics for HNTs dispersion in the composites. Possible applications for this work is needed for wider industrial applications as in the medical fields. The future work is open for more experimental work that includes TPU as a host material and HNTs as additives to create varieties of composites that may have applications in many challenging fields. In order to achieve these targets, some recommendations are outlined such as a study on other mechanical properties such as fatigue life, in order to evaluate the viability of the composite.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.rinp.2018.02.008>.

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