Engineering Failure Analysis 35 (2013) 718–725

Contents lists available at ScienceDirect

Engineering Failure Analysis

journal homepage: www.elsevier.com/locate/engfailanal

Impact fracture behaviour of silane-treated halloysite nanotubes-reinforced unsaturated polyester

M.T. Albdiry *, H. Ku, B.F. Yousif

Centre of Excellence in Engineered Fibre Composites (CEEFC), Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba 4350, QLD, Australia

ARTICLE INFO

Article history:
Available online 17 July 2013

Keywords:
Halloysite nanotubes
Polyester
Impact property
Plastic deformation

ABSTRACT

This work investigates the effects of untreated and silane-treated halloysite nanotube (HNT) particles on the micromechanism of plastic deformation of unsaturated polyester (UP) nanocomposites under impact loading conditions. The impact fracture properties of the prepared materials were characterised based on the temperature range of −20 to +60 °C using falling weight impact tester. The chemically-modified halloysite with silane coupling agent (s-HNT) showed less hydrophilic towards the polyester matrix, thereby a good interfacial adhesion and uniform structures of HNT in the matrix are obtained compared to the untreated. The incorporation of both unmodified and modified HNT particles up to 5 wt.% into the UP revealed a modest increase in the impact strength and total energy of nanocomposites, since the well dispersed particles in the matrix hindered the crack propagation under the impact loading. SEM examinations revealed that the fracture mode on UP surface was a smooth fast brittle while, the nanocomposite surfaces showed a sign of plastic deformation.

Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

1. Introduction

It is well recognised that unsaturated polyester (UP) resins are mostly used in automobile and boats components, pipes and tanks, building panels, and so forth due to their ease in processing, low viscosity, good chemical and corrosion resistance, and high performance to cost ratio [1]. However, the generation of a three-dimensional crosslinking structure in the UP from a free-radical copolymerization between low molar mass that possesses several covalent C=C bonds and the monomer (solvent) typically styrene results in localised plastic deformation in front of the crack tip, leading to catastrophic brittle failure [2]. Hence, much work has been done on thermoset polymers (e.g., epoxy, phenolic, unsaturated polyester) in order to reduce their brittleness and the damage severity without sacrificing their strength and stiffness. Thus, various synthetic fibres (glass, carbon, kevlar, etc.) have been and continuously used in producing good mechanical properties composite materials with low cost and light weight. However, several drawbacks may accompany with manufacturing of fibre-polymer composites, since they need to be laid up one-by-one and being isolated by a layer of matrix, thereby long and well bonded fibres have to be guaranteed otherwise, the weak adhesion at the interface induces poor reinforcement and subsequent reduction in the stress-transfer between the fibres and the polymer matrix [3], Also, the weak in out-of-plane direction when compared with in-plane direction and the anisotropic behaviour of the laminate composites are other issues associated with fibre-polymer composites [4]. Since the emerge of nanotechnology and nano-reinforcements (e.g. carbon nanotubes, nano-SiO_2, nano-Al_2O_3 nanocrystalline metals, nano-TiO_2, nanoclay and most recently halloysite nanotubes) have steered the orientation of the literature onto polymer nanocomposites to be one of the most popular areas for materials' development [5,6].

* Corresponding author.
E-mail address: Mushtaq.Albdiry@usq.edu.au (M.T. Albdiry).

1350-6307/$ - see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.engfailanal.2013.06.027

Many diverse investigations cover a broad range of topics including structure–property relationship; composite reinforcement, non-reinforcement (flame resistance, barrier properties) and so forth have been conducted. Among them, some of preliminary studies have been addressed the impact resistance of polymer-based nanocomposites. From which, there is no clear evidence describing the role of nanoparticles on the energy dissipation and material resistance under impact loading. For instance, Yuan and Misra [7] examined the micromechanism of plastic deformation under impact loading of polypropylene (PP)/clay nanocomposites at temperature range of −40 °C to +70 °C. It was found that the impact strength in the range of 0 to +70 °C increases with the addition of nanoclay into PP composite due to the change in the primary mechanism of plastic deformation from crazing and vein-type in neat PP to microvoid-coalescence-fibrillation in the nanocomposites. Lin [8] characterised the fracture behaviour under impact loading of three different polymer matrices (polyacrylate (PA), polyimide (PI), and polypropylene (PP)) reinforced with silicate layers. The results showed that the interfacial crack area in low energy impact was reduced for all silica-filled composites due to the interfacial reaction that provided an effective barrier for advancing cracks. Meanwhile, PA/30 wt.% silica had the best structural stiffness among others. In terms of using multi-walled carbon nanotubes to enhance toughening and the load-carrying capability of PP composites, Zhang et al. [9] showed that the impact resistance is highly temperature-dependent, since it considerably improved at a temperature above the glass transition temperature of the neat PP. Besides, it was observed that the impact behaviour varies with the length of nanotubes; the longer the nanotubes the higher toughening efficiency at temperature above the T_g.

Despite the abovementioned literature on the impact strength of polymer nanocomposite, this property however, has not been profoundly studied. Thus, there is a need to investigate the effect of internal structure morphology and the external environments on the impact fracture toughness in polymer nanocomposites. Therefore, this study is motivated to study the effect of HNT concentration and HNT modification using vinyltrimethoxysilane coupling agent on the impact fracture behaviour of UP–HNT/s-HNT nanocomposites. Moreover, the relationship between the morphological structure and the total energy absorption under impact loading in the temperature range of −20 to + 60 °C is addressed.

2. Experimental

2.1. Materials and samples preparation

Unsaturated polyester resin (UP, AROPOL®-1472PLSE, Nupol, Australia) contains 45% styrene, and its catalyst Methyl Ethyl Ketone Peroxide (MEKP/Butanox-M50) contains 33% peroxide were utilised as polymer matrix. Halloysite nanotubes with an average length of 1.5 μm, exterior diameter of 60 nm, and internal diameter of 20 nm supplied by Applied Minerals, USA were used as the reinforcement nano-filler.

Vinyltrimethoxysilane-98% solution (VTMS, $C_5H_{12}O_3Si$) with molecular weight of 148.23 purchased from Sigma, Aldrich was used as coupling agent to improve the dispersibility of HNT particles in polymer matrix. Before the preparation of nanocomposites, halloysite particles were chemically treated with VTMS solution with a ratio (1:10) of HNT particles i.e., 10 ml of VTMS and 100 g of HNTs were added to an aqueous solution in a glass beaker containing 500 ml of ethanol absolute, 50 ml of distilled water and 2 ml of acetic acid to maintain PH value around the range of 4.5–5.5. The solution was prepared using sol–gel process on a hotplate magnetic stirrer at temperature of 60 °C for 2 h. Thereafter, the slurry was separated from the distilled water and poured into flat glass pans for drying under a fuming hood at ambient temperature for 2 h and in oven at 100 °C for 8 h until the moisture is fully evaporated. The dried particles were grounded using a porcelain mortar and pestle to crush the bulk agglomerates and the ground particles were then screened with a fine metal sieve.

In the preparation process of the polymer nanocomposites, various concentrations (1–9 wt.%) of untreated halloysite (HNT) and silane-treated halloysite (s-HNT) particles were incorporated into the UP resin to produce UP/HNT and UP/s-HNT nanocomposites by using mechanical stirrer and ultrasonication process at ambient temperature. Then, the catalyst MEKP was added to the mixture with a percentage of 1% of UP and stirred again before poured in the moulds. The samples were initially cured at room temperature for 24 h and post cured at 60 °C for 2 h followed by 90 °C for 2 h in an oven. Upon completion of curing, the specimens were removed from the moulds and cut to the impact samples required in this experiment. The neat UP samples were prepared following an identical curing process as baseline for comparing the results.

2.2. Characterizations

The impact testing of the neat UP and UP-based untreated and silane-treated HNT nanocomposites were conducted by using INSTRON Dynatup model 8200 with a dropped weight of 2.84 kg from 1 m height at 2.9 m/s impact velocity. The impact samples with final dimensions of $6 \times 25 \times 150$ mm^3 were cut and the impact strength is performed for at least three samples for each nanocomposite systems at a range of temperatures (−20 to +60 °C). Additional information for the materials tested including total impact energy, load–time–energy characteristics, and deflection at peak load were automatically measured and recorded from the Dynatup machine.

In order to further understanding of the role of untreated and silane-treated HNT particles on the morphological characteristics for UP/HNT and UP/s-HNT composites, the dispersion status of HNT particles were examined using transmission

electron microscope (TEM, JEOL-1010) at an acceleration voltage of 100 kV. Furthermore, the mode of fracture mechanism under impact loading on the reinforcement of UP with HNT particles was identified by using scanning electron microscope (SEM, Philip XL-30).

3. Results and discussion

3.1. Impact testing

Figs. 1 and 2 show the impact strength and the total energy of unfilled UP and its nanocomposites as a function of different concentrations of pristine HNT and testing temperatures (−20, +20, and +60 °C). It can be observed from the figures that both the impact strength and the amount of energy absorbed by specimens during the entire impact test (total energy) are modestly increased with the addition of HNT up to 5 wt.% in all testing temperatures. However, further addition above this content lower the impact strength due to the particles clustering and poor interactions between the UP and HNT particles. This finding is in agreement with Lin et al. [10] who reported an improved impact strength by 300% in nanocomposite on reinforcement polystyrene (PS) with 5 wt.% HNT particles, but further addition of HNT decreased the impact strength of PS/HNT nanocomposite considerably. Along with this, it can be also observed from the figures, a moderate increase in impact strength and total energy of nanocomposites with increasing testing temperature. Indeed, the manner in which is upon the increase of HNT loading, the ductile–brittle transition temperature (T_{db}) increases making the material more brittle below this transition. Increasing the testing temperature improves the interfacial strength and hence resulting in better toughening criterion [11]. Also, the impact behaviour is highly temperature-dependent, at sub-zero temperature and room temperature all materials especially thermosets, presented a brittle manner that was characterised with an abrupt breakage after reaching peak values of impact load since they cannot absorb a considerable amount of energy before they fail. Comparatively, obvious crack propagation took place within the samples that impacted at higher temperatures (60 °C) which approximated to the glass transition temperature (T_g) of the UP so that the test time (or fracture deflection) was dramatically prolonged [12]. The T_gs of the neat UP and its nanocomposites based on untreated HNT obtained from differential scanning calorimetry (DSC) are given in Table 1.

In additions, the surface treatment of halloysite particles with VTMS silane solution has slightly improved the impact strength and total energy of nanocomposites as shown in Figs. 3 and 4, respectively. This increase may be attributed to the improved interfacial adhesion between s-HNT and the UP matrix due to the chemical treatment which can act to prevent the propagation of cracks generated during the impact test. Better interfacial bonded materials require higher energy absorbing capacity which in turn lead to higher impact strength [13]. For instance, the impact strength of nanocomposite increased by 11% on the reinforcement of UP matrix with 3 wt.% HNT and increased by 16% with the incorporation of the same amount of s-HNT particles i.e., the impact strength rose from 3.09 kJ/m^2 for the unfilled UP to 3.45 and 3.6 for UP/3 wt.% HNT and UP/3 wt.% s-HNT, respectively. Morote-Martinez et al. [14] believed that the addition of nanosilica to the UP resin imparts higher shear thinning index (STI) value which results in higher pseudoplasticity and better impact strengths. Furthermore, it was found that the addition of silane-treated nanosilica gives thixotropy to the UP resin and improved rheological properties due to the low primary particle size of the nanosilica that contains siloxane and silanols groups on their surface, thereby gives higher impact energy values. Further, it is deduced that the uniform distribution and well dispersed of HNT particles in the UP matrix (Fig. 5) may influence the deformation behaviour towards a higher energy absorption by activating localised cavitational craze-like and shear yielding mechanisms.

However, the further addition of halloysite and the increased surface reactivity may also increase the tendency to particle agglomeration. The impact strength decreased from 3.09 kJ/m^2 to 2.4 and 2.5 kJ/m^2 with the introduction of 9 wt.% HNT and 9 wt.% s-HNT, respectively. Moreover, the addition of nanofiller into polymers particularly thermosets obviously reduced the

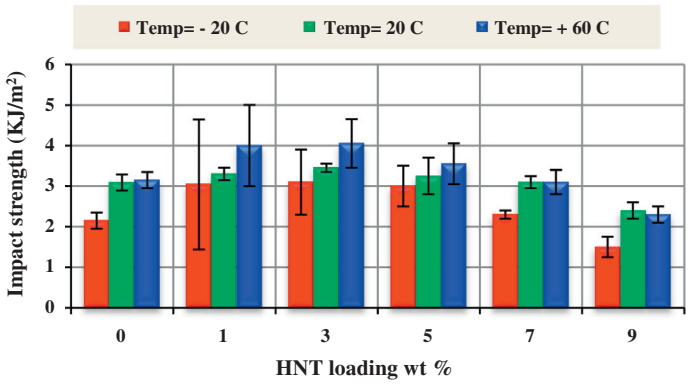

Fig. 1. Comparsion of impact strength for the neat UP and its nanocomposites as function of untreated halloysite and temperature.

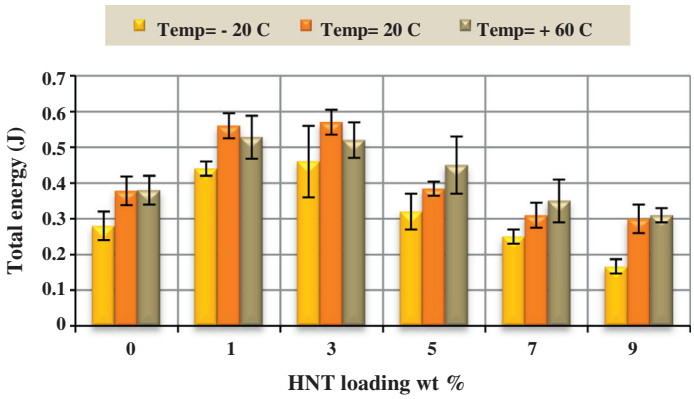

Fig. 2. Variation of total energy of neat UP and its nanocomposites based on untreated halloysite and temperature.

Table 1
Glass transition temperatures of untreated HNT filed UP nanocomposites.

Materials	T_gs obtained from DSC
Neat UP	60.2 ± 1.8
1 wt.% HNT/UP	55.6 ± 2
3 wt.% HNT/UP	54.2 ± 0.9
5 wt.% HNT/UP	53.8 ± 1.6
7 wt.% HNT/UP	53 ± 1.2
9 wt.% HNT/UP	52.8 ± 1.9

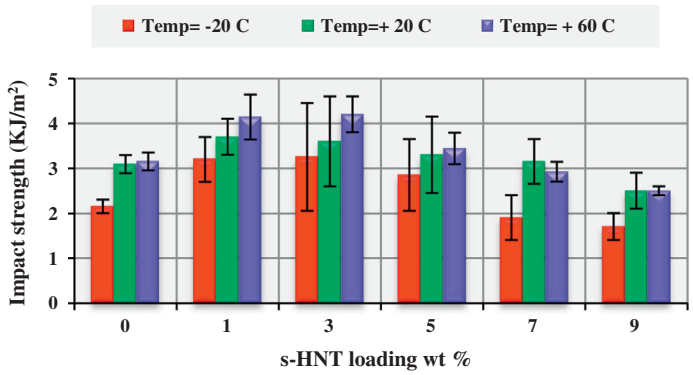

Fig. 3. Impact strength of the neat UP and its nanocomposites as function of silane-treated (s-HNT) loading and temperature.

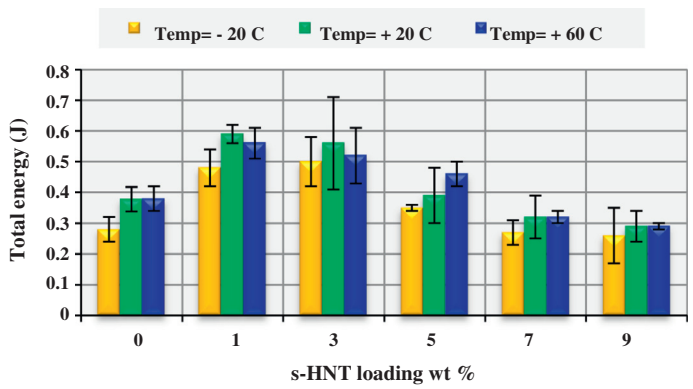

Fig. 4. Variation of the total energy of the neat UP and its nanocomposites based on silane-treated (s-HNT) loading and temperature.

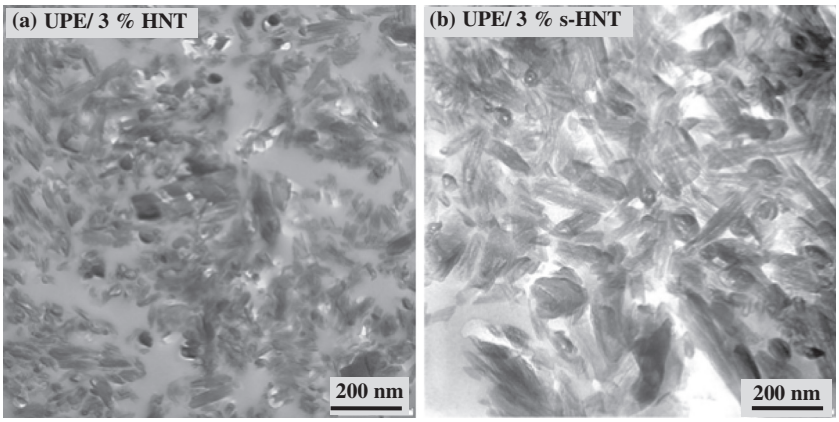

Fig. 5. TEM micrographs of UP/3 wt.% HNT and UP/3 wt.% s-HNT nanocomposites.

brittleness and toughening characteristics since the highly crosslinked network of thermoset are very sensitive to notches and local inhomogeneities. The higher concentrations of particles may agglomerate and act as stress concentrators and subsequently reduced absorbed impact energy of the composites may occur.

3.2. Morphology

Fig. 5 illustrates transmission electron microscopy (TEM) micrographs of nanocomposites based on UP filled by 3 wt.% untreated halloysite (HNT) and 3 wt.% silane treated halloysite (s-HNT) particles. It can be observed from the figure that the morphological structures of both nanocomposites based on reinforcement UP resin with HNT and s-HNT particles prepared by mechanical stirrer and ultrasonication are uniformly dispersed. Moreover, the role of chemical silane treatment on the hydrophilic HNT surface contributed in the rearrangement and delamination of HNT particles in the UP matrix with no entanglement as depicted in Fig. 5a. However, rich/poor regions of nano-reinforcements in the matrix appeared, especially

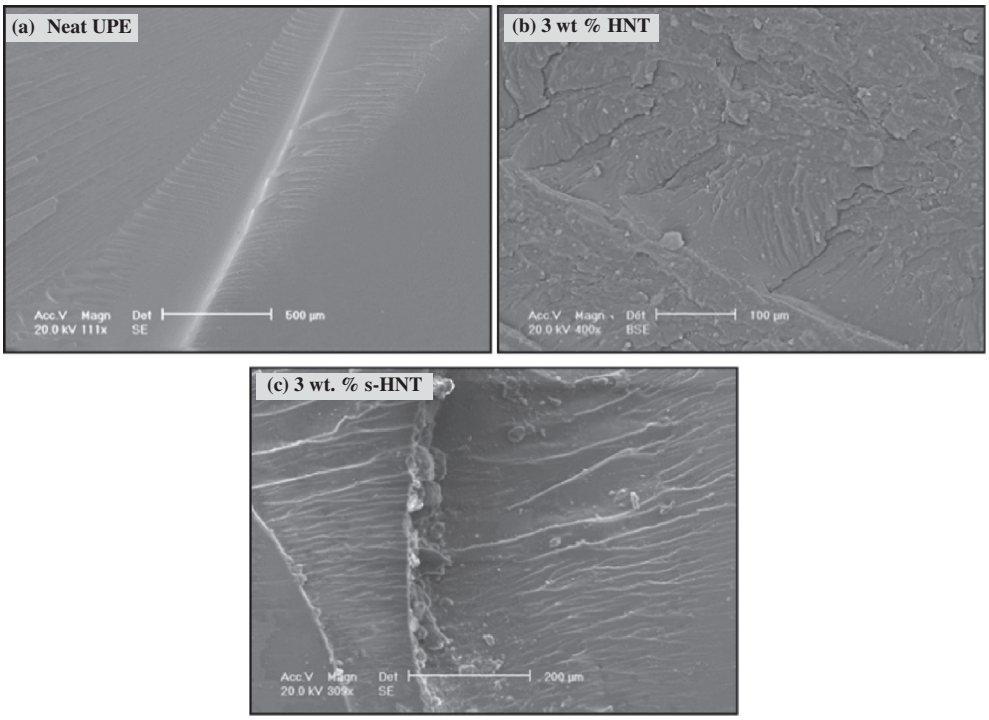

Fig. 6. SEM micrographs of the surface fracture of (a) the neat UP, (b) nanocomposite containing 3 wt.% HNT, and (c) nanocomposite containing 3 wt.% s-HNT particles impacted tested at 20 °C.

with the further increase of halloysite content in the polymer matrix. This phenomenon was attributed to the insufficient time of mixing since the mixing was the same for all nanocomposite systems. The higher additions of HNT showed to be mixed for longer time in order to achieve uniform dispersion through the polymer matrix [15].

The morphology of impacted fracture surfaces of the specimens is examined by scanning electron microscopy (SEM) to identify the fracture mode of the neat UP and its nanocomposites under impact loading at the microscopic level. Fig. 6 shows the SEM micrographs of the neat UP and UP/3 HNT and UP/3 s-HNT nanocomposites deformed by falling weight at room temperature (20 °C). It revealed that the fracture surface of the unfilled UP impacted samples (Fig. 6a) was smooth (fast brittle fracture mode) i.e., no energy can be absorbed by the resin. On the other hand, the nanocomposites samples containing HNT particles (Fig. 6b) or s-HNT (Fig. 6c) showed a little plastic deformation in the fracture surface since the particles may hinder the crack propagation in the composite. However, the high strain rate of dropped tip of the tup in the impact machine and the dense crosslink UP network tend to reduce the extent of plastic deformation which in turn resulting in decreased impact strength. In the mean time, the shear yielding mechanism is an energy absorption mechanism associated with

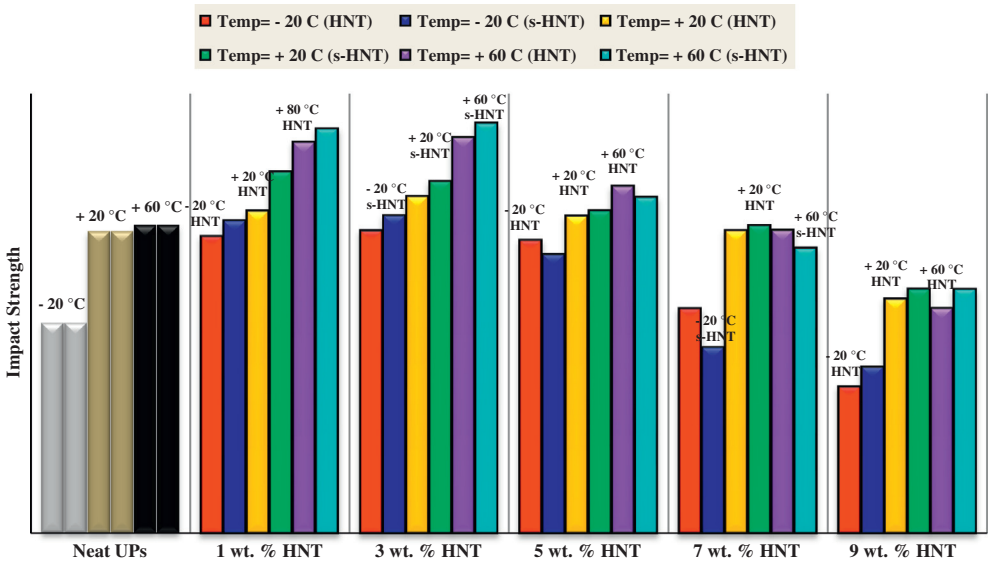

Fig. 7. Variation of impact strengths of the neat UP and its nanocomposites as function of halloysite loadings, HNT and s-HNT and different temperatures (−20, +20, and +60 °C).

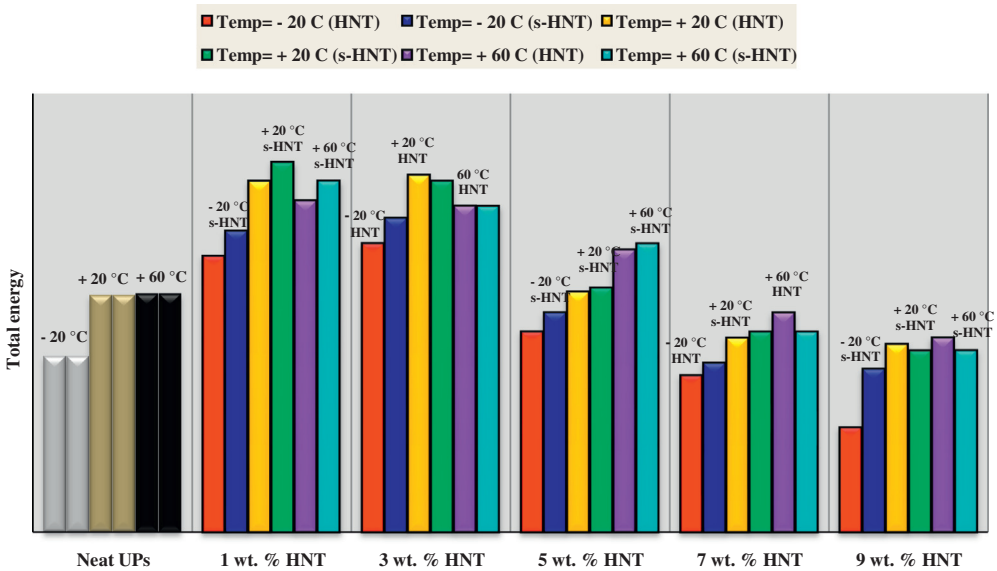

Fig. 8. Total energy of the neat UP and its nanocomposites with different halloysite, untreated and silane-treated particles and different temperatures.

nanocomposites containing modified halloysite filled UP matrix (Fig. 6c). Such plastic flow might spread shear bands in the whole sample absorbing a significant quantity of energy or might tend to localised yielding resulting in isolated shear bands. The manner of such phenomenon is again due to the surface modification of halloysite with silane as coupling agent, resulted in good interfacial adhesion and uniform morphological structures, while the impact resistance of particulate-filled polymer composites depends on the presence and shape of stress concentrators and molecular properties [16]. Furthermore, Figs. 7 and 8 show the variation of impact strengths and total energies of UP and its nanocomposites. These provide a further understanding on the role of introducing unmodified and silane-modified HNT particles in UP nanocomposites.

Generally speaking, in the neat thermosets, the impact toughness and molecular aspects of craze/yield behaviour are controlled by two parameters: entanglement density and the characteristic ratio of the chain. Increasing the crosslink density lowers the impact fracture toughness at any given temperature by shifting the T_g upward, and limiting the total crack-tip strain that can be realised, while high crosslink density systems were found to be unresponsive to rubber toughening at any temperature since the distance (molecular weight) between crosslink is proportional to the toughenability of the system. Whereas, the impact toughness and brittle–ductile transition (BDT) are related to the filler shape, content, particle size, size distribution, and its dispersion in the matrix in particulate filled polymer composites. Producing an inhomogeneous structure and loosely bonded material resulted in increased brittleness. Although, many studies have been practiced to impart ductility or increased impact strength of thermosets usually by blending them with impact modification, namely reactive (flexibilizers or elastomers) or nonreactive (plasticizers); the toughening mechanisms and the impact fracture behaviour of the thermosets are not a well-understood phenomenon [17,18].

4. Conclusion

The aim of this research is to identify the impact performance of the neat UP and its nanocomposites based on different concentrations of unmodified halloysite (HNT) and silane-modified (s-HNT) particles using a falling weight tester. The impact strength was conducted in the temperature range of −20 °C to +60 °C in order to determine the correlation between microstructural and impact strength under different particle loadings. The following points can be concluded the results:

- All materials were fast shatter when impacted at sub-zero temperatures. However, increasing the impact testing temperatures to approximate T_g of the polymer matrix improves the interfacial strength that affect the ductile–brittle transition temperature (T_{db}), and hence, better impact strengths with acceptable toughening criterion can be obtained.
- The impact strength and the total energy that absorbed by specimens before failure are slightly increased with the addition of both unmodified HNT and silane-modified HNT particles up to 5 wt.% for all testing temperatures. However, the further addition of nanoparticles the lower impact strength due to particle clustering and the poor interactions between the UP and HNT particles.
- According to SEM observations, the addition of HNT into the UP matrix is associated with change in fracture from cleavage and fast brittle fracture in the neat UP to microvoid-coalescence with a minor plastic deformation in nanocomposites. Moreover, TEM micrographs showed a uniformly distributed structure, specifically nanocomposite contains silane-modified HNT particles which in turns resulted in tightly bonded and tougher materials in the inter-particle regions and this may also improves the impact properties of nanocomposites.

Acknowledgments

The authors wish to thank Applied Minerals, USA for free of charge providing of halloysite nanotubes. M. Albdiry would like to acknowledge the financial assistance from the University of Southern Queensland and his supervisors.

References

[1] Pascault J-P, Sautereau H, Verdu J, Williams RJ. Thermosetting polymer. New York: Marcel Dekker, Inc.; 2002.
[2] Young RJ, Lovell PA. Introduction to polymers. Florida, (USA): Taylor & Francis Group; 2011.
[3] Banea MD, Silva LFMd. Adhesively bonded joints in composite materials: An overview. Proc Inst Mech Engrs. Part L: J Mate Des Appl 2009;223.
[4] Gibson RF. Principles of composite material mechanics. UK: CRC Press; 2007.
[5] Paul DR, Robeson LM. Polymer nanotechnology: nanocomposites. Polymer 2008;49:3187–204.
[6] Albdiry M, Yousif B, Ku H, Lau K. A critical review on the manufacturing processes in relation to the properties of nanoclay/polymer composites. J Compos Mater 2013;47:1093–115.
[7] Yuan Q, Misra RDK. Impact fracture behaviour of clay-reinforced polypropylene nanocomposites. Polymer 2006;47:4421–33.
[8] Lin J-C. Investigation of impact behaviour of various silica-reinforced polymeric matrix nanocomposites. Compos Struct 2008;84:125–31.
[9] Zhang H, Zhang Z. Impact behaviour of polypropylene filled with multi-walled carbon nanotubes. Eur Polym J 2007;43:3197–207.
[10] Lin Y, Ng KM, Chan C-M, Sun G, Wud J. High-impact polystyrene/halloysite nanocomposites prepared by emulsion polymerization using sodium dodecyl sulfate as surfactant. J Colloid Interface Sci 2011;358:423–9.
[11] Yuan Q, Misra RDK. Polymer nanocomposites: current understanding and issues. Mater Sci Technol 2006;22:742–55.
[12] Friedrich K, Fakirov S, Zhang Z. Polymer composites: from nano-to-macro-scale. (USA): Springer Science & Business Media, Inc.; 2005.
[13] Deng S, Zhang J, Ye L. Halloysite-epoxy nanocomposites with improved particle dispersion through ball mill homogenisation and chemical treatments. Compos Sci Technol 2009;69:2497–505.
[14] Morote-Martinez V, Pascual-Sanchez V, Martin-Martinez JM. Improvement in mechanical and structural integrity of natural stone by applying unsaturated polyester resin-nanosilica hybrid thin coating. Eur Polym J 2008;44:3146–55.

[15] Albdiry MT, Yousif BF. Morphological structures and tribological performance of unsaturated polyester based untreated/silane-treated halloysite nanotubes. Mater Des 2013;48:68–76.
[16] Nelson JK. Dielectric polymer nanocomposites. NY (USA): Springer science; 2010.
[17] Huang Y, Hunston DL, Kinloch AJ, Riew CK. Mechanisms of toughening thermoset resins. In: Riew CK, editor. Toughened plastics I. Washington (DC): American Chemical Society; 1993. p. 1–35.
[18] Srivastava I, Koratkar N. Fatigue and fracture toughness of epoxy nanocomposites. JOM 2010;62:50–7.