

University of Southern Queensland



**Role of Silanised Halloysite Nanotubes on the
Morphological and Materials Characteristics of Thermoset
Composites**

A thesis submitted by

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Abstract

The effects of nano-reinforcements on the material characteristics of thermoset nanocomposites in relation to their different morphological structures are not yet well understood. This study investigates the effects of untreated halloysite (HNT) and vinyltrimethoxysilane (VTMS)-treated halloysite nanotubes (s-HNT) on the morphological and materials characteristics of highly crosslinked unsaturated polyester (UPE) nanocomposites. The grafting of the VTMS coupling agent on the halloysite surface was performed using the sol-gel process. Nanocomposites based on different weight percentages (1 wt % to 9 wt %) of HNT or s-HNT were prepared via high shear disperser, followed by the ultrasonication technique.

The morphological structures and dispersion of halloysite particles in the UPE matrix were examined using transmission electron microscopy (TEM), and wide-angle and small-angle x-ray scattering (WAXS and SAXS). Fourier Transform Infrared (FT-IR) spectroscopy was used to determine the molecular structures and indicate the vibrational states of the chemical bonds obtained after curing. Thermogravimetric analysis (TGA) was applied to detect the thermal stability, and differential scanning calorimetry (DSC) spectra were applied to measure the glass transition temperature (T_g) in heating mode. The viscoelastic properties—the storage modulus (E'), loss modulus (E'') and $\tan(\delta)$ —were measured using dynamic mechanical analysis (DMA).

Mechanical properties viz. tensile strength, Young's modulus, elongation at break, flexural strength and modulus of the developed materials were determined. The elastic modulus was predicted using different mathematical models—the Halpin-Tsai, Smallwood-Einstein, Kerner, and Guth and Gold models—in order to further understand the correlation between the mechanical properties and the morphology.

The tribological performance of neat UPE and different nanocomposite systems was also explored. Wear resistance was evaluated using block-on-ring (BOR) configuration against a stainless steel counterpart under dry sliding conditions with

different operating parameters. The topography analysis of worn surfaces was examined using scanning electron microscopy (SEM) analysis to determine the wear mechanisms occurring in such materials.

The micromechanism of plastic deformation of neat UPE and its nanocomposite systems was characterised under impact loading conditions. The impact strength and total energy were performed with a falling-weight impact tester at different temperatures (-20 °C, +20 °C and +60 °C). The morphologies of tensile-fractured surfaces and impacted-fractured surfaces of unfilled UPE and UPE filled with HNT and s-HNT nanocomposites were identified to delineate their fracture modes.

The fracture toughness measurements represented by the critical stress intensity factor (K_{Ic}) and critical strain energy release rate (G_{Ic}) were calculated based on linear elastic fracture mechanics (LEFM) and two different geometries tested under two different loading conditions: a single-edge notch (SEN) specimen under three-point bending (SEN-3PB) and a compact tension (CT) specimen under tension. The crack initiation and propagation phenomenon were simulated using a traction-separation cohesive element method via ABAQUS finite element (FE) software. The SEM observations were used to identify the roles of HNT and s-HNT particles in toughening mechanisms and initiating plastic deformation in the nanocomposites.

The results showed that the surface of s-HNT was rougher than the untreated HNT particles due to the presence of multiple interfacial bonding sites on the silanised surface, which induced better adhesion and load transfer among the interface regions. A more well-dispersed structure with less skewed-like aggregates was observed in the UPE/s-HNT over the UPE/HNT composites. The incorporation of HNT or s-HNT particles into the UPE nanocomposites changed their crystalline structure, indicating a high degree of nanotube orientation.

The FT-IR spectra of the s-HNT powder exhibited that the Si-O-Si absorption band occurred in the region of 701 to 1,085 cm^{-1} wavenumbers. No significant change in the thermal stability of the nanocomposites was observed with the use of silane-treated nanoparticles. The effect of HNT or s-HNT on the T_g values was relatively insignificant, while they slightly reduced with increasing halloysite concentrations.

This was likely because coupling of halloysite to the polymer through adsorption and hydrogen bonding led to strengthening the interface and reducing the T_g values.

All material properties—such as tensile and flexural strength, impact strength and fracture toughness—except wear resistance, exhibited a steady-state increasing trend with the incorporation of up to 5 wt% HNT or s-HNT into the UPE resin. The 3% HNT/UPE or 3% s-HNT/UPE nanocomposites were found to obtain the highest values of these properties supported with uniformly dispersed particles. It was also proven that the computational results of damage zone and unstable crack propagation validated by the cohesive element method were convergent with the experimental data.

Compared to the HNT, the addition of the same content of s-HNT particles indicated slightly higher strength and toughness owing to the well-dispersed silanised particles and the enhanced interfacial adhesion thereof on initiating/participating in plastic deformation in the nanocomposites. Further increase of halloysite, irrespective of whether they were untreated or silane-treated, showed gradual decreases in most material properties associated with the presence of large clusters in the UPE nanocomposites.

The SEM observations of the fracture surfaces showed brittle fast fracture for neat UPE and coarser surfaces with different energy dissipation mechanisms for the nanocomposites. With the introduction of untreated halloysite, zone shielding and shear yielding mechanisms with the presence of full particle debonding—which activates void expansion and matrix shear deformation—were observed and suggested to be responsible for the toughness improvement in the the UPE/HNT nanocomposites. In addition, other major mechanisms—massive shear banding, crack deflection and local plastic deformation—occurred around the crack initiation zone, while river line patterns, a tail-like structure and the formation of microcracks mechanisms were observed in the UPE/s-HNT nanocomposites.

Certification of Dissertation

I certify that the thoughts, experimental work, numerical outcomes and conclusions reported in this dissertation ‘**Role of Silanised Halloysite Nanotubes on the Morphological and Materials Characteristics of Thermoset Composites**’ are entirely my own efforts, except where otherwise acknowledged. To the best of my knowledge, I also certify that the work presented in this thesis is original, except where due references are made.

.....

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List of Abbreviations

3-D	three-dimensional
3PB	three-point bending
BOR	block-on-ring
CNT	carbon nanotube
COD	crack opening displacement
CoF	coefficient of friction
CT	compact tension
DBTT	ductile-brittle transition temperature
DCZM	discrete cohesive zone model
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
EDS	energy-dispersive spectroscopy
EDX	energy-dispersive x-ray
EPDM	ethylene propylene diene monomer
FE	finite element
FT-IR	Fourier Transform Infrared
HNT	halloysite nanotube
LEFM	linear elastic fracture mechanics
MEKP	Methyl Ethyl Ketone Peroxide
MMT	montmorillonite
MPS	γ -methacryloxypropyl trimethoxysilane
MWCNT	multi-wall carbon nanotube
NS	nanosilica
PES	polyethersulphone
PNC	polymer matrix-based nanocomposite
PP	polypropylene
PPA	phenylphosphonic acid
PS	polystyrene
SAXS	small-angle x-ray scattering
SEM	scanning electron microscopy

SEN	single-edge notch
SEN-3PB	single-edge notch under three-point bending
SENB	single edge notch bending
s-HNT	silanised halloysite nanotube
SS	stainless steel
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
UPE	unsaturated polyester
US	United States
VCCT	virtual crack closure technique
VTES	vinyltriethoxysilane
VTMS	vinyltrimethoxysilane
XFEM	extended finite element method
XRD	x-ray diffraction
WAXS	wide-angle x-ray scattering