



Development and characterization of halloysite nanotubes reinforced polyetherimide (PEI) nanocomposites

Abrar Ahamad, Dhananjay Singh and Pradeep Kumar*

Department of Chemical Engineering, Institute of Engineering and Technology, Lucknow-226 021, Uttar Pradesh, India

E-mail: pradeepkumar@ietlucknow.ac.in

Manuscript received online 01 May 2020, accepted 01 June 2020

Nanocomposites comprising of polyetherimide (PEI) incorporated with various loadings (1, 2 and 3) wt% of halloysite nanotubes (HNT's). The developed PEI/HNT's nanocomposites were characterized by UTM, TGA, SEM and FTIR. The mechanical properties of the developed nanocomposites have shown an appreciable enhancement in tensile and toughening properties. The maximum enhancement was found at 2 wt% loading of HNTs in PEI matrix nearly 8% enhancement in tensile stress, 4% modulus, 40% impact energy and 43% izod impact strength as compared to pure PEI. Thermo-gravimetric analysis (TGA) result of prepared nanocomposites shows that there is an increase in the temperature of 20°C in thermal stability with the addition of 2 wt% HNT's in PEI matrix. SEM studies reveal that PEI matrix possesses excellent dispersion of HNTs. The possible interaction between PEI and HNTs was investigated by Fourier Transform Infrared Spectroscopy (FTIR) which confirms the better activity of HNT's in PEI matrix.

Keywords: Halloysite, PEI, tensile properties, TGA, morphology.

Introduction

In the field of aerospace, aviation, automobile and machinery the high performance thermoplastics polymers, blends, composites and nanocomposites materials containing inorganic nanofiller playing an important role of replacement of metallic materials due to rapid growth of technology and their excellent improvement in thermal and physical properties^{1,2}. Composite are the new types of materials having two different phases, one phase called matrix phase and the second phase is disperse phase. The properties of matrix phase and dispersed phase are totally different from each other. Nanocomposites material is a type composite material which having at least one of the phases in the range of nanometer scale (i.e. ≤ 100 nm). Thermoplastics polymer nanocomposites comprise of 2 phases in which first is matrix phase (polymer) and another is dispersed phase (nanofiller). The properties of matrix phase (polymer) dramatically improve due to very low loadings of nanofiller^{3,4}. Studies on polymer nanocomposites have nowadays a great attention due to the enhancement of various multifunctional properties. Recently, most of the polymer researchers is con-

centrating on the polymeric nanocomposite material with improving thermo-mechanical, electrical resistance and EMI shielding properties^{5,6}.

PEI is a high performance thermoplastic amorphous polymer. It is mostly utilized in the field of special applications like aerospace, automotive, and micro-electronics due to having lower thermal expansion and better mechanical, chemical and electrical properties. The PEI is homogeneous polymer having a glass transition temperature (T_g) of 490 K and having a thermal stability in the range of cryogenic temperature (CT) to 623 K. PEI consist of ether groups are also responsible for a certain chain flexibility and hence, it shows good processability. Due to having excellent processability characteristics, it can be processed by using various techniques such as injection molding, injection stretch blow molding, and extrusion molding process. PEI is having characteristics of fire resistant property with low amount of smoke emission. In addition PEI is also having high Young's modulus. Several other properties such as thermal, mechanical, morphological and electrical can be modified by incorporating adequate amount of nanofiller⁷. The pellets of PEI mixed

with halloysite nanotubes (HNTs) using melt extrusion technique enhances the properties of PEI over other nanofillers⁸.

The prime aim of the HNTs loading in PEI is to assist the transfer of load from specific matrix matter to the nanofiller. In order to developed high-performance nanocomposites of HNTs and PEI factors such as surface modification, homogeneous dispersion and orientation of HNTs must be control. The HNTs are extracted from natural resources in the form of aluminosilicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) having hollow nano-tubular structure^{9,10}. HNTs containing different mineral composition, tetrahedral structure and unique reinforcing ability on various polymers properties hence, it is utilized as a supplement polymer. Low cost of HNTs shows an alternative role for the development of high-quality nanocomposites compared to other costly nanofiller like CNTs^{11,12}. Uses of developed PEI based nanocomposites reinforced with HNTs are in the industrial, defense, aircraft, automobile and railways sectors.

The prime goal of our research work is to prepared light-weight multifunctional materials for advanced applications. The influence of various loadings of HNTs on various properties of PEI such as thermal stability, phase morphology, tensile, percentage elongation, modulus and izod impact, are point out in this research work.

Experimental

Materials used:

PEI (Utem-1000) having glass transition temperature ($T_g \sim 490$ K), molecular weight (592.6 g/mole), MFI (9.0 g/10 min) and specific gravity of 1.27 g/cm³ at ambient temperature and was procured from Sabic Innovation Plastic (USA). The HNTs having specific gravity 2.54 g/cm³ was supplied by Sigma-Aldrich (USA) and having purity greater than 98%.

Nanocomposites preparation:

Before compounding of PEI and HNTs, the pellet of PEI (Utem-1000) has been kept at 353 K in oven under vacuum for 8 h of time to remove moisture content. After drying, the PEI has been mixed with HNTs in varied loadings (1, 2, 3 wt%) as mentioned in Table 1. The homogeneous mixture of HNTs and PEI are fed into co-rotating twin screw extruder for melt extrusion process. The different zones temperature (feed, compression, metering and die zone) of extruder were maintained between 593–653 K and speed of screw is kept

at 90 rpm. After that the extrudate is converted in the form of pellets with help of pelletizer machine. The samples for analyzing the test have been prepared by Electronica injection molding machine. The different zones barrel temperature (hopper to nozzle) has been maintained at 603 K, 623 K, 643 K, 663 K at 30 mm/s injection speed.

Testing and characterization:

Mechanical testing:

Mechanical testing is determined as per ASTM D638 standard using specimens with dumb-bell shape. Tensile properties (Tensile stress at maximum load, Young's modulus and Elongation at break) have been tested by INSTRON Universal Testing Machine (UTM) with a gauge length of 0.050 m and crosshead speed of 0.005 m/min at ambient temperature. Impact strength of developed nanocomposites was evaluated by impact tester as per standard of ASTM D-256 at ambient temperature. The size of izod impact test specimens is 64×12.7×3.2 mm.

Thermogravimetric analysis:

The degradation behavior and thermal stability PEI/HNTs nanocomposites was carried out by Perkin-Elmer thermogravimetric analysis (TGA). The thermal degradation of nanocomposite has been recorded in the temperature range from 50 to 800°C with constant heating rate of 10°C/min and 20 ml/min N₂ flow rate.

Scanning electron microscopy:

Before scanning electron microscopy (SEM) analysis the specimen surfaces of tensile test have been coated with gold sputtering to enhance the emission of secondary electrons. The morphology of fractured surface has been analyzed through SEM, JEOL Japan.

Fourier Transform Infrared spectroscopy:

The functional groups and possible interaction between PEI, HNTs in PEI/HNTs nanocomposites have been analyzed by Fourier Transform Infrared spectroscopy (FTIR), Agilent (Cary 600).

Results and discussion

Mechanical testing:

Mechanical properties results such as elongation at break, Young's modulus, tensile stress, and impact strength of PEI/HNTs nanocomposites are shown in Figs. 1, 2 and 3. It is

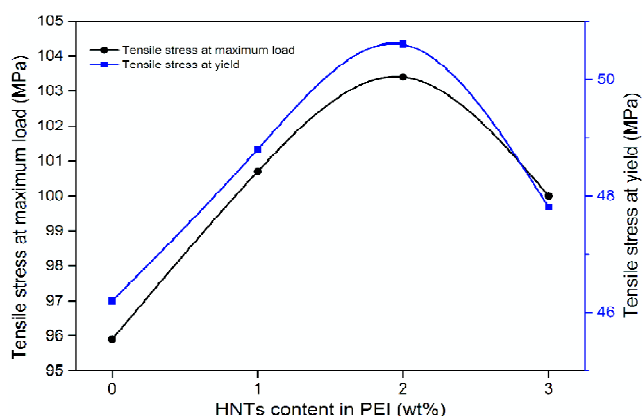


Fig. 1. Variation of tensile stress at maximum load and yield with varied loadings of HNTs.

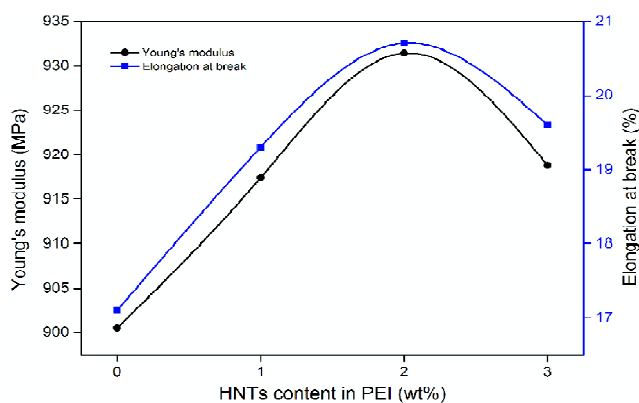


Fig. 2. Variation of modulus and elongation at break with varied loadings of HNTs.

clear from the Figs. 1-3 mechanical properties of developed nanocomposites improved by increasing the HNTs content up to 2 wt% and then decreases at 3 wt%. The enhancement of 5%, 8% and 5% in tensile stress at maximum loads in developed nanocomposites at (1, 2, 3) wt% of HNTs loadings respectively compared to pure PEI matrix is due to transfer of stress from matrix to nanofiller. The effective stress transfer from matrix to nanofiller depends on the uniform and homogeneous dispersion of nanofiller and also on the interfacial interaction between PEI and nanofiller. One more cause for the improvement of tensile stress is that the penetration of PEI inside the tubular structure of HNT's and forms inter-tubular interactions. Decrease in tensile properties after 2 wt% in PEI matrix as depicted in Fig. 1 is due to clustering of HNTs nano-particles. The clustering of HNTs was clearly visible in SEM images as shown in Fig. 5(e). It is notable point that the slippage at the polymer-filler interface lowers the stress transfer ability because of higher strain. Slippage of polymer-filler interface is decrease because of the HNTs nano-particles, which cause for the enhancement of mechanical properties at 2 wt% addition of HNTs. A similar enhancement is arises in case of tensile stress at yield also. From Fig. 2, it is found that 4% improvement in Young's modulus of PEI/HNTs nanocomposite materials at 2 wt% HNTs compared to pure PEI. The addition of micro and nanofiller as reinforcement, impart more stiffness compared to PEI cause of improvement of modulus properties¹³.

It is clearly evident from Fig. 3 the impact energy and

ized impact strength have found maximum at 2 wt% loading of HNTs in PEI matrix. An enhancement of 40% and 43% in impact energy and izod impact strength compared with pure PEI matrix respectively. This is due to the development of strong and tough nanocomposites with the addition of HNTs. Therefore, increase in impact strength may be due to increasing toughening property of HNTs in PEI matrix¹⁴. A better interfacial interaction between PEI and HNTs may also convey to enhancement on impact energy as well as impact strength. Good HNTs dispersion and uniform distribution in PEI matrix may also provide greater impact strength at 2 wt% HNTs content as shown in Fig. 3. Therefore, it can be concluded that the improvement in mechanical properties of developed PEI/HNTs nanocomposites is due to the uniform dispersion and excellent interfacial interactions.

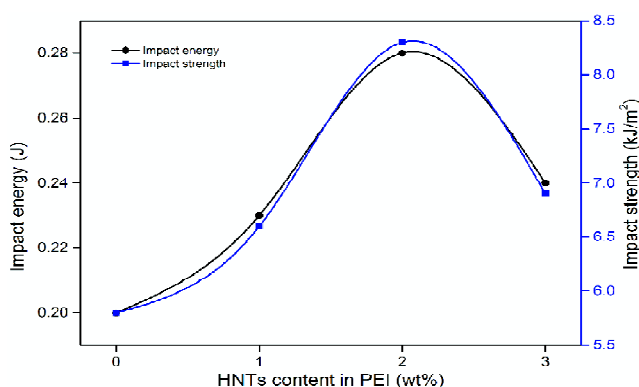


Fig. 3. Variation of impact energy and izod impact strength with varied loadings of HNTs.

Table 1. Compounding formulation of PEI and HNTs in varied loadings

Sr. No.	Sample code	PEI (wt%)	HNTs (wt%)
1.	PH0	100	–
2.	PH1	100	1
3.	PH2	100	2
4.	PH3	100	3

Thermogravimetric analysis:

Thermal stability and degradation behavior of PEI and PEI/HNTs nanocomposites has been accessed by TGA as shown in Fig. 4. It is evident from Fig. 4 that PEI nanocomposites at 2 wt% of HNTs have shown the greater thermal stability over the other composition in whole temperature. Table 2 considers the results related with TGA analysis. This Table 2 indicates that 5% weight loss of 1 wt% of HNTs content is at 549°C which is slightly higher than that of pure PEI. But in case of 2 wt% loading of HNTs the thermal stability improves 567°C (5% weight loss), which is 20°C

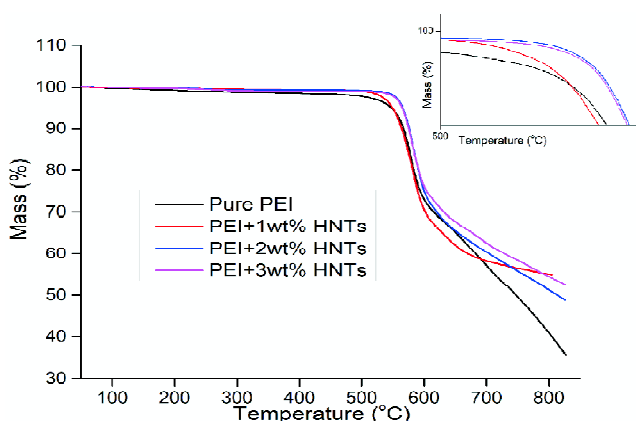


Fig. 4. TGA thermo-grams of PEI nanocomposites with varied loadings of HNTs.

Table 2. Thermal stability of PEI nanocomposites with varying HNTs loading

Sample code	Temperature (°C)	
	5% weight loss	10% weight loss
PH0	547	564
PH1	549	563
PH2	567	576
PH3	563	572

greater than that of pure PEI. In addition to, a similar result has been found in case of 10% weight loss shown in Table 2. With the 2 wt% HNTs content a large number of restricted sites are formed which resist the chain mobility and decreases the thermal vibration of C-C bond¹⁵. Therefore, large amount of energy required to degrade on PEI matrix which cause of the increase in thermal stability of developed nanocomposites materials. Because of uniform and homogeneous dispersion of HNTs, the more number of restricted sites in 2 wt% of HNTs content as compared other samples (i.e. 1 and 3 wt% of HNTs). Thus, the inclusion of inorganic components HNTs into PEI matrix can improve their thermal stability of nanocomposites materials.

Scanning electron microscopy:

The state of homogenous dispersion of nanofiller in a polymer matrix is known to be a key part for improving the mechanical properties of nanocomposites¹⁶. The reduction in mechanical properties is because of the agglomerated nanofiller and this increases the stress concentration in the polymer matrix. This problem is quite challenging when nano-particle are utilized as filler because nano-particles have strong tendency to agglomerate. So, uniform and homogeneous dispersion of nano-particles in polymer matrix is a tough task.

The surface morphology of PEI/HNTs nanocomposites has been analyzed by SEM technology and the respective micrographs are shown in Fig. 5(a-e). Fig. 5(a) shows the SEM micrograph of pure HNTs. SEM micrographs shows that most of the samples having cylindrical tubes which are 30–40 nm in diameter and 0.5–2.5 microns in length. The dispersion of HNTs is poly-dispersed in length. There is huge difference among all prepared samples is the average domain size. In Fig. 5(c), smaller domain size can be seen clearly. The decrease in average domain size might be attributed to uniform dispersion of the HNTs in PEI matrix¹⁷. These results are in excellent confirmation to the previous investigation. The average domain size of PEI nanocomposites at 3 wt% loading of HNTs is larger as compared to the average domain size of PEI nanocomposites at 2 wt% of HNTs as shown in Figs. 5(e) and 5(d) demonstrates respectively. The larger particle size of PEI nanocomposites at different loading (1 and 3 wt%) of HNTs attributed to the poor interfacial adhesion. The PEI nanocomposite at 2 wt% of HNTs has smallest average particle size as compared to 1

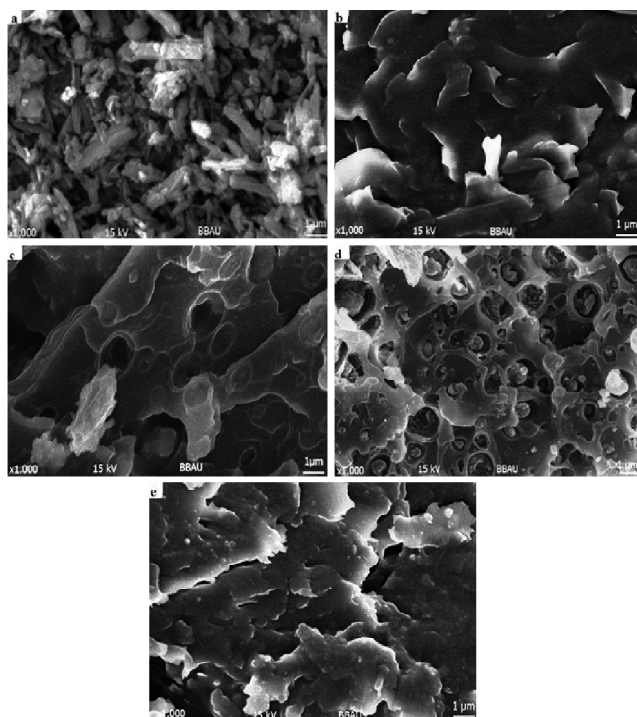


Fig. 5. SEM images of: (a) pure HNTs, (b) pure PEI, (c) PEI+1 wt% of HNTs, (d) PEI+2 wt% of HNTs and (e) PEI+3 wt% of HNTs.

and 3 wt%. Therefore, it can be concluded that there is excellent adhesion and dispersion of HNT's at 2 wt% in PEI matrix.

Fourier Transform Infrared Spectroscopy (FTIR):

The FTIR spectra of pure PEI, HNT's and PEI/HNTs nanocomposites materials are shown in Fig. 6 (a-c). The peaks around 3693 cm^{-1} and 3623 cm^{-1} in HNT's is denote to stretching vibrations due to outer and inner hydroxyl (-OH) groups. The characteristic peak at 1647 cm^{-1} and 1000 cm^{-1} in HNT's spectra is related to the stretching vibrations of the carbonyl group (C=O) and stretching vibrations of Si-O bonds, respectively. The stretching vibrations of the carbonyl group (C=O) at 1647 cm^{-1} appear in nanocomposites of PEI/HNT's as shown in Fig. 6(c). In addition to this, the (-OH) peaks of HNT's at 3693 cm^{-1} and 3623 cm^{-1} disappear with the addition of PEI with HNT's, as depicted in Fig. 6(b, c). The peak 1716 cm^{-1} correspond to C=O peak of imides group of pure PEI has replaced with greater value in PEI/HNT's (1720 cm^{-1}). The peak 2923 cm^{-1} arises in PEI matrix corresponds to -CH stretching which disappear in PEI/HNTs (Fig. 6(a, c)). This confirms that there is a possible

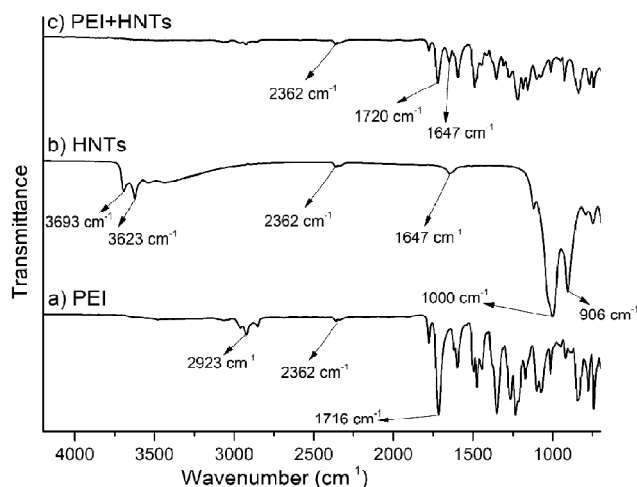


Fig. 6. FTIR spectra of: (a) pure PEI, (b) HNTs and (c) PEI/HNTs.

interaction between PEI and HNT's. The peaks 2362 cm^{-1} appear by default in all three samples correspond to the CO_2 background.

Conclusions

PEI nanocomposites filled with HNTs have been developed and their mechanical, thermal and morphological properties have been characterized by using various advanced analytical techniques, i.e. UTM, TGA, SEM, and FTIR. The enhancement in the mechanical properties at 2 wt% of HNT's in PEI matrix was obtained. The increment of 8% in tensile stress at maximum load, 4% in Young's modulus, 40% impact energy and 43% izod impact strength are found compared to pure PEI matrix. It is also evident from TGA thermograms that there is maximum improvement in thermal stability is 20°C at 2 wt% loading of HNT's. The SEM micrographs reveal that uniform dispersion of HNTs (2 wt%) are found better over the entire PEI matrix. Because of homogeneous dispersion of HNTs all the mechanical properties and thermal stability improves. The possible interaction of functional group of PEI and HNTs confirms by FTIR analysis. Therefore, it can be concluded that appreciable enhancement are found at 2 wt% loading of HNT's in PEI matrix.

References

1. M. Díez-Pascual, M. Naffakh, C. Marco, G. Ellis and M. A. Gómez-Fatou, *Progress in Materials Science*, 2012, **57(7)**, 1106.
2. H. Song, N. Li, Y. Li, C. Min and Z. Wang, *Journal of Materials Science*, 2012, **47(17)**, 6436.

Ahamad *et al.*: Development and characterization of halloysite nanotubes reinforced polyetherimide *etc.*

3. N. Maity, A. Mandal and A. K. Nandi, *Polymer*, 2016, **103**, 83.
4. S. Mondal and A. Kumar, *Journal of Materials Science: Materials in Electronics*, 2018, **29(16)**, 14122.
5. F. Akbar, M. Kolahdouz, S. Larimian, B. Radfar and H. Radamson, *Journal of Materials Science: Materials in Electronics*, 2015, **26(7)**, 4347.
6. T. Wang, L. Yuan, G. Liang and A. Gu, *Applied Surface Science*, 2015, **359**, 754.
7. A. M. Diez-Pascual, M. Naffakh, C. Marco and G. Ellis, *Composites Part A: Applied Science and Manufacturing*, 2012, **43(4)**, 603.
8. T. S. Gaaz, A. B. Sulong and A. A. H. Kadhum, *Sains Malays*, 2016, **45**, 1235.
9. T. S. Gaaz, A. B. Sulong, M. N. Akhtar and M. R. Raza, *International Journal of Automotive & Mechanical Engineering*, 2015, 12.
10. T. S. Gaaz, A. B. Sulong, A. A. H. Kadhum, M. H. Nassir and A. A. Al-Amiery, *Science of Advanced Materials*, 2017, **9(6)**, 949.
11. U. A. Handge, K. Hedicke-Höchstötter and V. Altstädt, *Polymer*, 2010, **51(12)**, 2690.
12. T. S. Gaaz, A. B. Sulong, A. A. H. Kadhum, A. A. Al-Amiery, M. H. Nassir and A. H. Jaaz, *Molecules*, 2017, **22(5)**, 838.
13. S. Y. Fu, X. Q. Feng, B. Lauke and Y.-W. Mai, *Composites Part B: Engineering*, 2008, **39(6)**, 933.
14. S. Deng, J. Zhang, L. Ye and J. Wu, *Polymer*, 2008, **49(23)**, 5119.
15. G. C. Nayak, R. Rajasekar and C. K. Das, *Journal of Applied Polymer Science*, 2011, **119(6)**, 3574.
16. S. Rooj, A. Das, V. Thakur, R. Mahaling, A. K. Bhowmick and G. Heinrich, *Materials & Design*, 2010, **31(4)**, 2151.
17. R. M. Mishra, A. Ahamad, K. N. Pandey and J. S. P. Rai, *Indian Journal of Pure & Applied Physics*, 2019, **57(11)**, 846.