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Atomic Force Microscopy and Thermal Decomposition Behavior of Inorganic nanoparticle filled HDPE Nanocomposites

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Abstract: High Density Polyethylene (HDPE) reinforced inorganic aluminium nitride (AlN) nanoparticles samples containing 0-9.5 wt.% were fabricated by mechanical mixing process. The AlN nanoparticles dispersion in HDPE polymer matrix system were studied with Atomic force microscopy (AFM). For lower concentration (1 and 2.5 wt.%), the AlN nanoparticles was found to be likely dispersed in the HDPE matrix. However, the addition of higher concentration of AlN nanoparticles (> 2.5 wt.%) resulted in a markedly finer dispersion and good interfacial bonding between HDPE polymer matrix and AlN nanoparticles. Due to the homogenous dispersion of AlN nanoparticles in HDPE polymer matrix the adhesion between HDPE matrix and AlN nanoparticles is found to be excellent; this finding is in line with Field emission scanning electron microscopic (FE-SEM) results. The average size of the AlN nanoparticles was found ~10-25nm. The thermal decomposition behaviour of AlN / HDPE nano-composite system were investigated by thermo-gravimetric analyzer (TGA) with O_2 gas atmosphere under non-isothermal conditions. Inorganic AlN nanoparticles reinforcement enhanced the thermal stability of the prepared nano-composites. The activation energy (E_a) of the thermal decomposition process was examined in light of two different integral based iso-conversional methods viz., Horowitz-Metzger (HWM) and Tang approaches. The E_a as a function of fractional conversion α was calculated for 0-9.5 wt.% loadings of AlN / HDPE composites and found to vary between 220.71-278.84 kJ/mol by HWM method and ~219.89-277.43 kJ/mol by Tang method. The 'E_a' estimated by HWM and Tang methods are found to be in excellent agreement with each other.

Keywords: Inorganic nanoparticles, Nano-composites, Atomic force microscopy, Thermal decomposition, Iso-conversional methods, Activation energy.

Introduction

High Density Polyethylene (HDPE) is one of the engineering thermoplastics that has excellent physical and mechanical properties widely applicable in various packaging applications. Its marvellous features such as low cost and low energy demand for processing, resistance to abrasion and corrosion, regular chain structure and good mechanical properties make HDPE enlarge its application persistently[1- 4]. HDPE filled with inorganic particulate fillers, such as Al_2O_3, $CaCO_3$, micro-/nano-SiO_2, glass, layered silicates and carbon nanotubes are often added to develop polymer composites, which usually combine the advantages of their constituent phases.

Inorganic nanofillers reinforced thermoplastic nanocomposites have attracted great interest nowadays, in both industrial, biomedical and electronic packaging applications. Among the wide variety of inorganic fillers, aluminum nitride (AlN) nano-filler have received considerable interest as promising materials for microelectronic devices. AlN has many attractive physical, thermo-mechanical and electronic properties, such as excellent thermal conductivity, good thermal stability, high electrical resistivity, high mechanical strength, low coefficient of thermal expansion (CTE), and relatively low cost[5-7]. It has therefore attracted extensive interest for applications as an electronic packaging material.

Over the past few decades, several researchers have paid attention to the mechanical and electrical properties of HDPE filled with carbon, graphite, MMT and aluminum nitride nanocomposites[1,7-9]. However, there are no sufficient literature and/or experimental results in the literature review about the effects of AlN nanofiller on the microscopic and thermal properties of AlN / HDPE nanocomposites for electronic packaging applications. The main objectives of the present investigation are in two folds; (1) fabricating of homogenous inorganic AlN nanoparticles / HDPE polymer nanocomposite, (2)studying the effects of inorganic AlN nanoparticles percentage on the microscopic and thermal behaviour of the HDPE nanocomposite.

Experimental

Materials

High density polyethylene (HDPE) used as base polymer in this study was of commercial grade (density of 0.95 g/cm^3) supplied by Loba Chemicals (India). The weight-average molecular weight (Mw) of this polyethylene is 132,000 g/mol and the poly-dispersity. Mw/Mn , is 13.3. The fine aluminium nitride (AlN) powder (density 3.26g/cm^3) used in this study was procured from Sky Spring nano, USA. As received xylene of Merck grade was used for homogenizing the HDPE and AlN mixture.

Nanocomposite Preparation

The procedure for preparation of pure HDPE and AlN / HDPE nanocomposites is shown in a flowchart given in Fig 1. Different weight % concentration of AlN nanofiller (viz., 0, 1, 2.5, 5.5, 7.5 and 9.5 wt.%) is mechanically mixed with appropriate quantity of HDPE powder. Firstly, the AlN nanofiller was premixed with calculated amount of xylene for 6 hrs to improve its dispersion capacity. With simultaneous stirring this premix was added very slowly into HDPE suspension. The suspension was stirred continuously with the help of a digital magnetic stirrer [Model: Heidolph MR 3001 K] in xylene for 8 hrs at 400 rpm, which results in homogeneous slurry of AlN / HDPE mixture. Then the slurry was further stirred with simultaneous heating at 130^{0}C for 6 hrs to evaporate xylene and moisture content (if present). Moreover, the heating is accompanied with vigorous magnetic stirring of the viscous fluid mixture to ensure a homogeneous distribution of AlN nanofiller. The process of heating and stirring is continued till xylene is completely evaporated. The resultant homogeneous mixture of HDPE and AlN is then slowly cooled down to room temperature. Both HDPE powder and AlN nanofiller were dried overnight at 140^{0}C prior to hot pressing. The resultant powder was further dried in oven at 110^{0}C for 6 hrs.

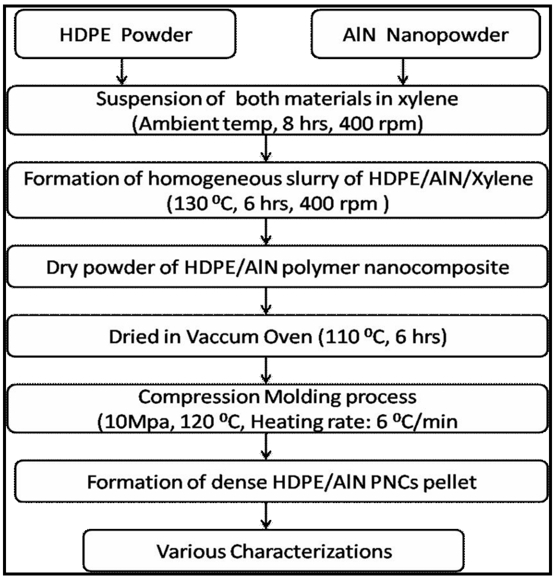

Fig 1. Schematic flowchart representation of the preparation process of novel AlN / HDPE polymer nano-composite (PNCs) .

Furthermore, the resultant powder were processed by compression molding process in a Carver press at a temperature of about 120^0C and a pressure of 10 Mpa. A laboratory hot press was used to fabricate the circular disk in a cylindrical chamber made of steel tool. The dried mixed powder of AlN/HDPE nanocomposite were filled in three pieces die. The AlN reinforced polyethylene mixture were placed in a mold that was positioned between two aluminum plates lined with aluminum foil. A mould release agent was used to prevent the HDPE melt from sticking to the die surface. Then the die was heated at an average heating rate of 6^0C/min to a maximum temperature of 120^0C. The pressure of 10 MPa was kept constant at 120^0C for 10 min and then, naturally cooled to below glass transition temperature of HDPE in a mould at an average cooling rate of 3^0C/min. Finally, the pellets were ejected out from the mold cavity. The size of molded disks was about 20 mm in diameter and 2 ± 0.5 mm in thickness. Additionally, these pellets were finished by abrading with emery papers and cleaned properly with acetone and dried. Fine pieces of solidified AlN / HDPE polymer nanocomposites were cut from the compression molded disks and then used for various microscopic and thermal characterizations.

Characterizations of the nanocomposites

The extent of AlN nanoparticle dispersion in HDPE polymer matrix was investigated by field emission scanning electron microscopy (FE-SEM) (JEOL JSM 6100 SEM). Cross sections of all compositions of nano-composites were cryo fractured in liquid nitrogen and then vacuum coated (2×10^6 Torr) with a thin gold film prior to the test.

The nanoscale morphology of inorganic AlN nanoparticles / HDPE composites were characterized with atomic force microscopy (AFM). All AFM images were captured in a scanasyst tapping mode by a Multimode 8 equipped with Nanoscope V convertor procured from Bruker (USA). A silicon tip (nominal radius 3nm) with a resonant frequency of about 150 kHz and a cantilever length of 253 µm was used. All the specimens scanning was performed in air at ambient temperature with scan angle 75^0 and scan rate of 0.9 Hz. The images (256 x 256 pixels) were recorded and analyzed using AFM software NanoScope version 1.20.

The thermal decomposition behaviour of various compositions of AlN / HDPE composite system have been investigated thermo-gravimetrically for nonisothermal conditions. The thermo-gravimetric analysis was performed with a Perkin Elmer Pyris Diamond TGA/DTA thermo-gravimetric analyzer. The AlN/HDPE samples (0-9.5wt.%) were analyzed at the heating rate of 5, 15, 25 and 35 ^{0}C/min. The initial mass of the sample was 11.0±0.27 mg. Samples are heated from room temperature to 700^0C. The experiments were carried out in a oxygen gas atmosphere with a flow rate of 50 ml/min and a purge time of 25 min.

Results and discussion

Microscopic investigations

Field Emission Scanning Electron Microscopy (FE-SEM) Analysis

To establish the dispersion characteristics of prepared inorganic nanoparticles (AlN) filled HDPE composites, the microscopic features of all samples has been observed using field emission scanning electron microscopy (FE-SEM). Fig. 2 shows the FE-SEM micrograph of 5. 5 wt.% AlN / HDPE nanocomposite. The fine dispersed spherical AlN nanoparticles appear as bright spots distributed in the dark HDPE polymer matrix (Fig. 2). The observed microscopic images revealed a good dispersion of inorganic AlN nanoparticles in the HDPE polymer matrix. It is well - known that most of the polymer nanocomposite properties are directly correlated to the distribution of nanoparticles into the polymeric matrix. In the present article, it was found that the AlN nanoparticles was homogenously distributed throughout the HDPE matrix. Therefore, the adhesion between HDPE polymer matrix and inorganic AlN nanoparticles is found to be admirable.

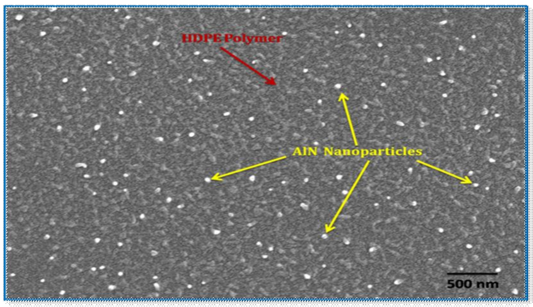

Fig 2. FE-SEM micrograph showing the morphology of 5.5 wt.% AlN / HDPE nano-composite.

Atomic Force Microscopy Analysis

The two dimensional AFM phase contrast images of 2.5, 5.5, 7.5 and 9.5 wt.% of the AlN / HDPE nanocomposite by intermittent tapping mode probe, after scanning a (2x2 μm^2) area is shown in Fig. 3(a-d). The phase images of the filled samples exhibit two shade difference: cyan coloured base for the polymer matrix and dark red spots on the surface of polymer matrix for AlN nanoparticles. The average size of the aluminium nitride nanoparticles is found to be ~10-25nm for various wt.% loading of AlN / HDPE composites.

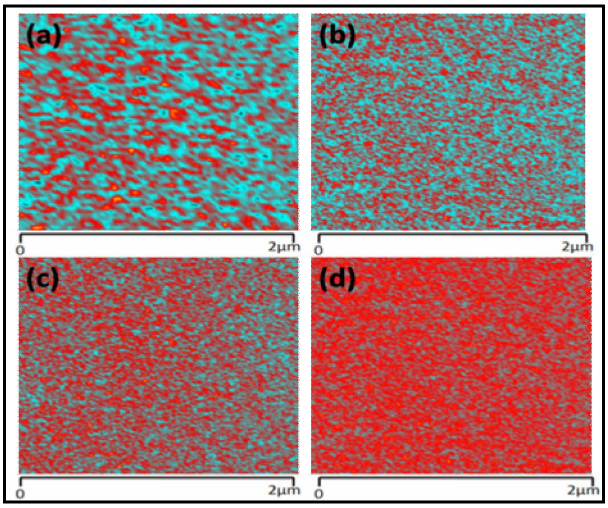

Fig 3. 2D AFM phase contrast images for AlN / HDPE nanocomposites recorded in Scan Asyst tapping mode, scanning area 2x2μm^2 for various wt.% loadings of AlN: (a) 2.5 wt.%, (b) 5.5 wt.%, (c) 7.5 wt.%, (d) 9.5 wt.%. The phase scale is 75^0 for every image.

Further, the height topography images are finely analyzed for calculating the roughness parameters viz., average roughness (Ravg) , root mean square roughness (Rrms) which indirectly indicate the extent of filler dispersion found ~ 0.40 - 4.78nm and ~ 0.98 - 4.93nm for 0 - 9.5 wt.% inorganic nanoparticle (AlN) loading which is shown in Table 1 respectively. The inorganic AlN nanoparticles size (diameter) were additionally analyzed and calculated the number-average particle diameter (Dn), weight-average particle diameter (Dw) and volume-average particle diameter (Dv) of 1-9.5 wt.% AlN / HDPE nanocomposites[10].

The number average particle diameter is determined from Eq. (1)

$$Dn = \frac{\Sigma NiDi}{\Sigma Ni} \qquad (1)$$

The weight average particle diameter is determined from Eq. (2)

$$Dw = \frac{\Sigma NiDi^2}{\Sigma NiDi} \qquad (2)$$

The volume average particle diameter is determined from Eq. (3)

$$Dv = \frac{\Sigma NiDi^4}{\Sigma NiDi^3} \qquad (3)$$

where, Ni is the number of nanoparticles having size (diameter) of Di. The determined inorganic AlN nanoparticle size (diameter) parameters Dn, Dw and Dv are summarized in Table 1 respectively.

Table 1. Roughness parameters and Particle size diameter measurement at nanometer range for AlN / HDPE nanocomposite.

Sample	Average Particle Roughness (Ravg) value (nm)	Root mean square Roughness (Rrms) value (nm)	Number-Average particle diameter (Dn)	Weight-Average particle diameter (Dw)	Volume-Average particle diameter (Dv)
Pure HDPE	0.40	0.98	-	-	-
HDPE+1.0 wt.% AlN	1.27	1.54	10.43	11.15	12.24
HDPE+2.5 wt.% AlN	2.16	2.73	12.76	13.03	14.66
HDPE+5.5 wt.% AlN	3.58	3.89	13.81	14.96	16.06
HDPE+7.5 wt.% AlN	4.12	4.21	15.78	16.77	18.38
HDPE+9.5 wt.% AlN	4.78	4.93	17.86	18.32	22.84

Interestingly, it have been found that, for lower concentration (1 and 2.5 wt.%), the inorganic nanoparticles was found to be likely dispersed in the HDPE polymer matrix. However, the addition of higher concentration of inorganic nanoparticles (>2.5wt.%) resulted in a markedly finer dispersion and good interfacial bonding between HDPE polymer matrix and inorganic nano-particles. Due to the homogenous dispersion of AlN nanoparticles in HDPE polymer matrix the adhesion between HDPE matrix and inorganic nanoparticles is found to be excellent; this finding is in line with field emission scanning electron microscopic results.

Thermal Decomposition Behaviour

Thermal stability analysis

Thermo-gravimetric analysis is carried out at multiple heating rates (viz., 5, 15, 25 and 35 ^{0}C/min) under oxygen gas atmosphere to find the thermal stability, thermal resistance and thermal decomposition kinetic behaviour of various concentration (0-9.5wt.%) of AlN / HDPE composites. TG-DTG thermograms of all compositions of inorganic nanoparticles (AlN) reinforced HDPE nanocomposites at a heating rate of 15^{0}C/min are shown in Fig 4.

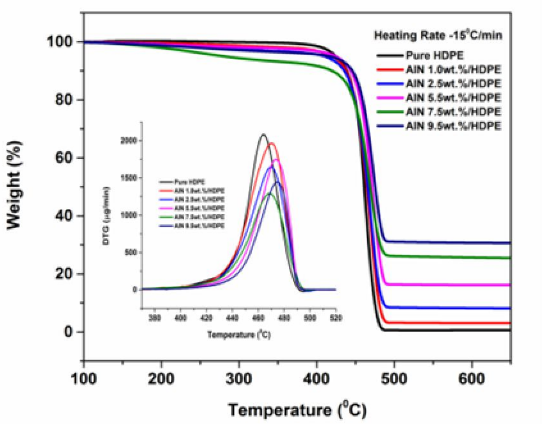

Fig 4. TG-DTG thermograms of various composition of AlN / HDPE nanocomposites at a heating rate of 15^{0}C/min.

The initial decomposition temperature (IDT) sometimes used to know thermal stability of materials is considered at which weight loss reaches 5%[11]. Temperature at 15% weight loss (T_{15}), Temperature at 25% weight loss (T_{25}), carboneous char (CC) and oxidation index (OI) of various wt.% loading of AlN / HDPE composites are given in Table 2. To compare the decomposition behaviours, along with other thermal decomposition properties Table 2 also lists the derivative peak rate (DTG peak temperature T_{max}) of decomposition of the AlN / HDPE composites.

Table 2. Thermal data obtained from TG-DTG thermograms of AlN / HDPE nanocomposites.

Sample	**IDT (^{0}C)**	**T_{15} (^{0}C)**	**T_{25} (^{0}C)**	**T_{max} (^{0}C)**	**Carboneous Char (CC)**	**Oxidation Index (OI)**
Pure HDPE	443	450	459	471	0.471	0.033
HDPE+1.0 wt.% AlN	445	453	461	475	2.891	0.201
HDPE+2.5 wt.% AlN	447	456	464	478	7.892	0.549
HDPE+5.5 wt.% AlN	449	458	467	480	14.781	1.029
HDPE+7.5 wt.% AlN	451	462	470	483	20.136	1.401
HDPE+9.5 wt.% AlN	454	465	474	487	26.739	1.861

It is observed that, with the incorporation of inorganic AlN nanoparticles into HDPE polymer matrix resulted in increase of thermal resistance (IDT). This might be due to the good adhesion between AlN nanoparticles and HDPE polymer matrix, obstructing the heat propagation thereby decreasing the decomposition rate. The T_{max} (DTG peak temperature), which is normally considered to understand the thermal stability of a material, [11] has been revealed improvement with the increase in inorganic AlN nanoparticles content. High heat energy is essential for filled nanocomposites to attain the same proportion weight loss than that is required for neat HDPE polymer. T_{15} and T_{25} results have shown trends analogous to that of IDT and T_{max}. T_{15} and T_{25} decomposition of AlN / HDPE nanocomposites is found higher than that of neat HDPE (Table 2). This can be attributed to the presence of inorganic nanoparticles , which has relatively higher thermal stability than pure HDPE. Carboneous char (CC) of AlN / HDPE nanocomposites at 550^{0}C have been found ~ 0.471- 26.739, increases with increasing inorganic nanoparticles (AlN) loading. Akheel Ahmed Syed et al. [12] reported that the increasing char yield is directly correlated to the strength of flame retardation. The average value of the oxidation index (OI) for the present composites lies between 0.033 and 1.861. This indicates that AlN / HDPE composites are thermally more stable than that of pristine HDPE.

Kinetic analysis of Thermal decomposition

Further, for thermal decomposition of polymeric materials, all kinetic studies employ the basic rate equation of fractional conversion ‘α’ given as:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(\frac{-E_a}{RT}\right) \qquad (4)$$

where, $\alpha = \left((W_0 - W_T)/(W_0 - W_f)\right)$ W_0, W_f are the initial, final sample weight and W_T is the weight of the sample at arbitrary temperature T. The overall reaction order is denoted by ‘n’, A is the pre-exponential factor (s^{-1}), E_a is the apparent activation energy of the degradation reaction (kJ/mol), R is the universal gas constant (8.314 J/mol K) and T is the reaction temperature respectively.

In the present article, the TGA curves at multiple heating rates viz., 5, 15, 25 and 35 ^{0}C/min were used to determine the decomposition kinetics for all samples under oxygen gas atmosphere. Two different integral based iso-conversional methods viz., Horowitz-Metzger (HWM) and Tang approaches is applied to calculate the kinetic parameters of prepared composites. HWM and Tang methods estimate the thermal degradation apparent activation energy (E_a) for all samples inbetween the conversion range $0.05 \leq \alpha \leq 0.95$ with multiple heating rates. For calculating E_a of the thermal decomposition process Horowitz-Metzger method[13] has been found to be the most versatile approach given by the following correlation:

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E_a\,\theta}{RT_{max}^2} + C \qquad (5)$$

where, T_{max} is the temperature at maximum rate of mass loss and α is the fractional conversion. Plot between $\ln[\ln(1-\alpha)^{-1}]$ versus θ produces a straight line. The activation energy (E_a) is calculated from the slope $\frac{E_a}{RT_{max}^2}$ of the best fitted lines.

Tang et al[14] developed a new accurate estimation of Arrhenius temperature integral using a two-step linearly fitting process that verified to obtain better accuracy in non-isothermal kinetic data. The final form of the associated iso-conversional expression, which is formulated for the TG analysis, acquires the following form:

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left(\frac{A*E_a}{Rg(\alpha)}\right) + 3.635041 - 1.894661\ln(E_a) - 1.001450\left(\frac{E_a}{RT}\right) \qquad (6)$$

At constant α, plot of $\ln\left(\frac{\beta}{T^{1.894661}}\right)$ versus (1/T) of Eq. 6 should give straight line, whose slope is used for estimation of the corresponding activation energy (E_a).

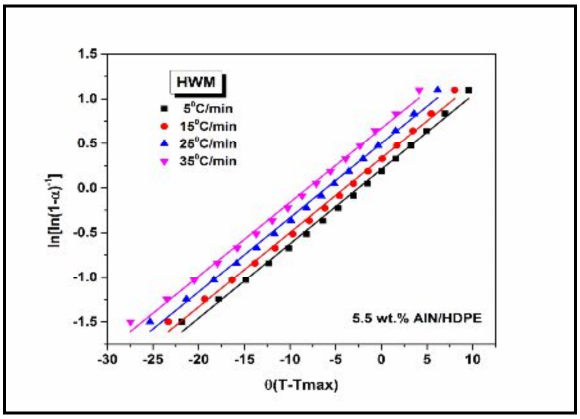

Fig 5. Plot of $\ln[\ln(1-\alpha)^{-1}]$ vs. $\theta(T-T_{max})$ using the Horowitz-Metzger method (HWM) for 5.5 wt.% AlN / HDPE nanocomposites at multiple heating rates viz., 5, 15, 25 and 35 ^{0}C/min.

The plots between $\ln[\ln(1-\alpha)^{-1}]$ versus θ (HWM) and $\ln\left(\frac{\beta}{T^{1.894661}}\right)$ versus (1/T) (Tang method) for various wt.% loading of AlN / HDPE composites inbetween the conversion range $0.05 \leq \alpha \leq 0.95$ under non-isothermal conditions have been shown in Fig. 5 and 6 respectively. The regression analysis gives the R^2, slopes and constants for each thermal decomposition process. The linear plots with regression coefficient (R^2) nearer to one have been opted for HWM and Tang methods.

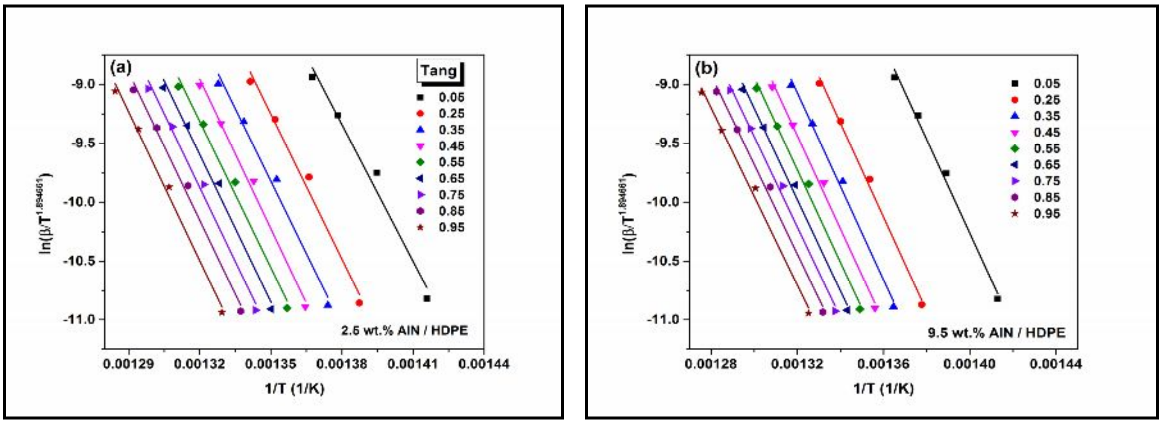

Fig.6. Plots of $\ln(\beta/T^{1.894661})$ vs. 1/T inbetween the conversion range $0.05 \leq \alpha \leq 0.95$ using the Tang method for 2.5 wt.% and 9.5 wt.% AlN / HDPE nanocomposites

The kinetic parameters including apparent activation energy (E_a) and regression coefficient (R^2) values evaluated for each thermal decomposition process and for each method (viz., HWM and Tang) have been tabulated in Table 3. Activation energy (E_a) values calculated by Horowitz–Metzger method range from 220.71 kJ/mol to 278.84 kJ/mol and that by Tang method are ranging from 219.89 kJ/mol to 277.43 kJ/mol.

Table 3. Activation energies calculated by Horowitz-Metzger (HWM) and Tang methods with respective correlation value (R^2) and Activation energy Deviation percentage values for AlN / HDPE nanocomposites.

Sample	HWM Method		Tang Method		Ea deviation % values
	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2	
Pure HDPE	220.71	0.995	219.89	0.996	0.371
HDPE+1.0 wt.% AlN	227.34	0.993	225.63	0.998	0.752
HDPE+2.5 wt.% AlN	239.81	0.998	238.05	0.995	0.733
HDPE+5.5 wt.% AlN	255.14	0.996	252.92	0.997	0.870
HDPE+7.5 wt.% AlN	267.92	0.995	265.34	0.996	0.963
HDPE+9.5 wt.% AlN	278.84	0.997	277.43	0.998	0.505

Both these kinetic theories have shown a increment in E_a values with the addition of inorganic AlN nanoparticles. The higher E_a values were observed for the entire single step thermal decomposition processes of AlN / HDPE nanocomposites (0 - 9.5 wt. %) estimated from HWM and Tang methods (Table 3). This may be due to at higher dosage of inorganic nanoparticles (AlN), higher energies might be required for bond scission and unzipping of crosslinked HDPE chains. Regression coefficient values of linear fit of the data according to Horowitz–Metzger method range from 0.993 to 0.998, whereas those for Tang method range from 0.995 to 0.998.

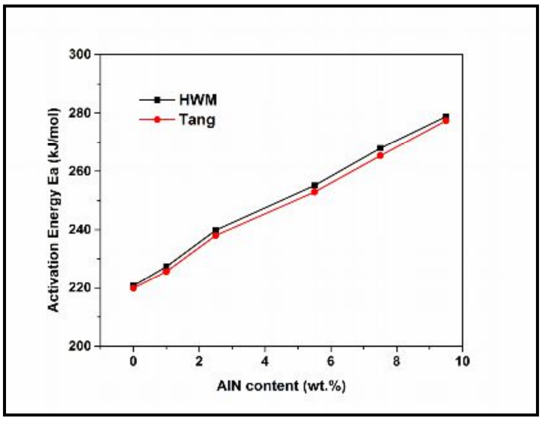

Fig 7. Activation energy (E_a) as a function of weight % of inorganic AlN nanoparticles in AlN / HDPE nanocomposites obtained by Horowitz-Metzger (HWM) and Tang methods.

In addition, the deviation (%) of activation energies based on HWM and Tang methods were also calculated. The E_a (deviation %) for pure HDPE and various compositions of AlN / HDPE composites (1-9.5 wt.%) are noticeable in Fig. 7 and Table 3 respectively. It have been found that the calculated deviation % of E_a for all samples were found within 1%. This suggests that HWM and Tang methods are more appropriate to describe for the thermal decomposition behaviour of AlN / HDPE nanocomposites. Hence, the 'E_a' estimated by HWM and Tang methods are found to be in excellent agreement with each other ; both the methods are absolutely acceptable for investigating the thermal decomposition behaviour of AlN / HDPE nanocomposites .

Conclusions

In the present study, AlN / HDPE nanocomposites with various concentrations of inorganic AlN nanoparticle content were prepared using mechanical mixing process. The field emission scanning electron microscopic analysis of all the samples revealed a homogenous distribution of inorganic AlN nanoparticles in the HDPE polymer matrix. Atomic force microscopy results revealed that nanoscale morphology and AlN nanoparticles dispersion was homogenous. Topographical roughness calculated for the composites using AFM increases with increasing AlN concentration. Microscopic studies confirms that with increasing the AlN nanoparticles content (> 2.5 wt.%) finer dispersion and good interfacial bonding of the inorganic AlN nanoparticles / HDPE polymer matrix have been observed. The thermal analysis results gives an insight that the thermal stability of prepared composites depend on the inorganic AlN nanoparticle concentration. The considerable increase in T_{max} and IDT from pure HDPE to AlN nanoparticles reinforced HDPE/ AlN composites during maximum rate of decomposition shows increase in thermal resistance. Apparent activation energy 'E_a' estimated by HWM and Tang methods inbetween the conversion range $0.05 \leq \alpha \leq 0.95$ with multiple heating rates under non-isothermal conditions are found to be in good agreement with each other. With increasing the AlN nanoparticles contents, the activation energy (E_a) of the nanocomposite increased. The possible reason behind it may be due to the increase in concentration of inorganic nanoparticles (AlN), higher energies might be required for bond scission and unzipping of crosslinked HDPE chains.

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