Thermal analysis of multi-walled carbon nanotubes doped glass fiber reinforced polymer composites

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Abstract Thermal characterization is one of the important aspects for evaluating the heat flux and decomposition kinetics of different materials, alloys and composites at different temperature. In this work Multi-scale nano-composites (MWCNTs/glass fiber/epoxy) were prepared by hand lay-up process followed by vacuum bagging method. Thermal properties of MWCNTs doped glass fiber reinforced polymer composites were evaluated by differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). It has been found that in the presence of MWCNTs it is very difficult to break the polymeric chains and that leads to reduction in cross linking density and glass transition temperature of MWCNTs doped glass fiber reinforced polymer composites as compared to pristine one.

Keywords: Thermal characterization; Nano-composites; Multiwall carbon nanotubes; Thermo-gravimetric analysis; Differential scanning calorimetry

1. Introduction

Generally composites have superior properties than that of metallic materials. Especially, glass fiber reinforced polymer is widely used by many industries due to its high specific strength, low weight, low cost, high stiffness and corrosion resistance [1, 2]. Moreover, when carbon nanotubes are introduced into composite materials, it will further enhance the overall properties owing to high tensile modulus of carbon nanotubes. Carbon nanotubes may be of either single wall or multiwall in nature. These carbon nanotubes may be produced by arc discharging process, chemical vapour deposition method and laser ablation method. Multi-walled carbon nanotubes are widely used as first phase or second phase reinforcement in polymer composites in order to enhance the mechanical, chemical and electrical properties.

Thermal analysis is one of the important characterization for evaluating decomposition kinetics, thermal stability, enthalpy, heat flux and glass transition temperature of different materials, alloys and composites at different temperature. Thermal stability is very important for any materials, polymer or composites so that it can be used without degradation at certain temperature. Most common thermal analysis such as TGA, DSC and TDA are widely used for characterizing the polymeric materials [3]. Thermo gravimetric analysis (TGA) is used to measure change in weight % with respect to temperature. Degradation of the materials largely depends upon the material structure and heating condition. Thermo -gravimetric analysis is widely used in the field of characterization of different types of polymer nano-composites [4]. Differential scanning calorimetry (DSC) is used to find the
melting temperature and glass transition temperature. Glass transition temperature \((T_G)\) is closely related with mobility of polymeric chain which adjudicates the transition phase between glassy and rubbery polymeric state \([5]\).

Present work consists of different thermal analysis (TGA, DSC and DTA) of MWCNTs doped glass fiber reinforced polymer composites. This thermal analysis needs for encompasses the composite materials at a particular temperature without degradation.

2. Experimental

2.1 Materials
Plain weave glass fibers having a weight of 600 GSM were procured from M. S. Industries, Kolkata (India). Density of used glass fiber was 2540 kg/m\(^3\). Bisphenol-A diglycidyl ether (DGEBA) under trade name of Lapox (L-12) was used as a polymer matrix. Triethylene tetra amine based hardener (K6) was used as a hardener. Both materials were procured by Atul industries Ltd, Balasad, Gujrat (India). Multi-walled carbon nanotubes were produced by arc discharge method \([6]\) for used as second phase reinforcement.

2.2 Composite materials manufacturing
Multi-scale nano-composites were manufactured by hand lay-up process and followed by vacuum bagging technique. In hand lay-up process, pre-calculated amount of multi-walled carbon nanotubes were weighed and mixed with matrix material in a beaker by mechanical process. Then, hardener was blended in a beaker. Each laminates (280 x 240 mm\(^2\)) of glass fiber was impregnated with mixed materials with matrix and hardener in the mass ratio of 10: 1. Now each impregnated layers was placed one by one and consolidated by hand roller so that entrapped air and extra resin can be removed. In this way total eight plies with different stacking sequence were made. In vacuum bagging method, first of all laminates was kept and seal properly inside the vacuum bag. Then, a pressure of 0.933 bar was applied in order to eliminate voids, entrapped air and extra resin. In the last, specimens were put under load for about 24 hours for complete the curing process.

2.3 Thermo-gravimetric (TGA) and differential thermal analysis (DTA)
Thermal analysis (TGA-DTA) was carried out to check the thermal stability and decomposition kinetics of MWCNT/GFRP samples from room temperature to 800\(^0\)C. TGA-DTA of samples were recorded on instrument with model no. NETZSCH Jupiter STA 449F3 in the temperature range of 0-800\(^0\)C. A sample size of 15.231 mg was taken and placed in alumina crucible with a heating rate of 10\(^0\)c/ minute, and heated in atmosphere of nitrogen having flow rate of 20 ml/minute.

2.4 Differential Scanning Calorimetry (DSC)
DSC analysis of different GFRP samples was carried out on instrument DSC Q10 V9.4 Build 287 in order to investigate the effect of temperature rise on polymeric/amorphous materials. Glass transition temperature \((T_G)\) was also evaluated from DSC curve to observe the effect of adding multi-walled carbon nanotubes in glass fiber reinforced polymer laminates. Aluminum pan was used for placing the samples which having weight of 1.556 mg. Heating rate was taken as 10\(^0\)c/ minute and nitrogen was used as a purge gas.

3. Results and Discussion

3.1 Thermo gravimetric analysis (TGA) for Laminates
TGA curves are used to evaluate the thermal degradation and thermal stability of constituent materials. TGA curves of pristine and MWCNTs doped GFRP laminates are illustrated in ‘figure 1’. Thermal degradation of materials largely depends upon the material structure and heating conditions. It can be demonstrated that thermal decomposition of each composite samples was taken place between 30\(^0\)C to
800°C.

Figure 1. TGA of neat and MWCNTs embedded GFRP laminates

Major degradation occurred almost in the range of 310-430°C. Substantial and minimum weight losses were found to be 21.2% and 13.4% for pristine GFRP and 0.5% MWCNT doped GFRP respectively. 1.25% MWCNTs doped GFRP revealed 18.36% weight loss, while 2% MWCNTs doped GFRP showed 14.44% weight loss. It can be construed that weight loss may be occurred due to thermal degradation of polymer matrix and glass fiber. It can be also delineated that, it is somewhat difficult to break the polymeric chains in the presence of multi-walled carbon nanotubes which leads to reduction in weight loss of MWCNT doped GFRP as compared to pristine GFRP. It can be also derived from TGA curve that between 420-800°C thermal degradation become stable. Rahman et al. [2] reported that thermal decomposition of neat woven glass fiber reinforced composite started earlier than CNTs grown woven glass fiber reinforced composite. However, Fawad Tariq et al. [7] reported higher weight loss in 0.25 wt% MWCNTs-CFRP as compared to neat carbon fiber reinforced polymer (CFRP) and construed that it may be occurred due to evaporation of residual solvent.

3.2 DTA analysis for laminates

DTA curve of pristine and MWCNTs doped GFRP laminates are illustrated in ‘figure 2’. All laminates have approximately coherent nature except 0.5 wt% MWCNTs doped GFRP laminates. However, this results doesn’t exhibit any significant peak corresponds to weight loss.
This is of particular interest, but for deeper look into that, it needs further investigation of subsequent derivatives [4].

3.3 DSC analysis for laminates:

DSC curve of MWCNTs doped GFRP is presented in ‘figure 3’, which clearly demonstrate that pristine GFRP and 2 wt% MWCNT doped GFRP have approximately akin heat flux profile. Coherent heat flux profile can be also seen for 0.5% and 1.25 wt% MWCNT doped GFRP. It can be derived from graph that 0%, 0.5%, 1.25% and 2 wt% MWCNTs doped GFRP have glass transition temperature of 340°C, 320°C, 300°C and 308°C respectively. This result shows that glass transition temperature of 0.5%, 1.25% and 2 wt% MWCNTs doped GFRP is found to be lower than that of pristine GFRP. It can be also deduce that more reduction in glass transition temperature (T_g) can be found for 1.25 wt% MWCNTs doped GFRP.

Basically, multi-walled carbon nanotubes are interrupted between the polymer molecular chains which restrain to make polymerization and cross linking. Therefore, it can be deduced that, reduction in glass transition temperature (T_g) for MWCNTs doped GFRP may be attributed to reduction in polymerization rate and cross linking density as well as due to pristine nature of multi-walled carbon nanotubes. It can be also observed that neat GFRP exhibited pronounce glass transition temperature as compared to others and this may be attributed to more cross linking formation among polymeric chains in the absence of multi-walled carbon nanotubes. Coherent heat flux profile has been reported by Rahman et al. [2] for neat and CNTs grown woven glass fiber reinforced epoxy composites. Nevertheless, they found some minor change in glass transition temperature (T_g) for CNTs grown woven glass fiber as compared to neat one. However, this results depict 5.88%, 11.76% and 9.41% change in glass transition temperature for 0.5%, 1.25% and 2 wt% MWCNTs doped glass fiber reinforced polymer composite as compared to neat one.
Figure 3. DSC of neat and MWCNTs embedded GFRP laminates

It can be envisaged that multi-walled carbon nanotubes may trap free radicals [8], resulting in reduction of cross linking density of epoxy resin, which actually incapacitate the polymer matrix interface. Rathore et al. [9] also reported reduction in glass transition temperature ($T_G$) for epoxy/0.1% MWCNT nanocomposite as compared to neat epoxy. It was construed that that MWCNTs may be penetrated into inter chain spacing of polymer that caused restriction in formation of cross linking which result in reduction in glass transition temperature ($T_G$).

4. Conclusions
Thermal behaviour of MWCNTs doped GFRP has been successfully studied. It was found that there was a reduction in weight loss of MWCNT doped GFRP as compared to pristine GFRP. This may be due to difficulty in breaking the polymeric chains in the presence of multi-walled carbon nanotubes. DSC analysis reveals that neat GFRP has a higher glass transition temperature than that of MWCNTs doped GFRP composites. This may be ascribed to interruption of MWCNTs between polymeric chains which restrict the mobility of polymeric chains. This causes reduction in cross linking density. DTA analysis doesn’t show any significant peak.

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