

Thermogravimetric Analysis (TGA) Study: Exploring the Reason of Increased Mass of CNF/PTFE Composite with Temperature at Higher Weights of CNF

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Abstract

CNF/PTFE composites of 3, 7, 10 and 26 wt% of CNF in PTFE were studied by TGA for their use as EMI shielding material. An abnormal slight increase in mass in TGA study has been observed at higher weight percent of CNF in composite samples. It is concluded that CO gas released in air ambient (Oxidative study) by PTFE contributes to increase the mass after heat treating the sample in Chamber. Few possibilities for increasing the mass regarding TGA systems have also been discussed.

Keywords: Carbon-nano-fibres (CNF), Nano composites, Thermogravimetric Analysis (TGA), Sintering

INTRODUCTION

TGA study on polymer/carbon nanotubes exhibited a higher temperature for the start of thermal degradation (i.e. improved thermal stability). The polymer nanocomposites of polyamide [1, 2], poly(dimethylsiloxane) [3], poly(methyl methacrylate) [4] and polypropylene systems [5] have supported the improved thermal stability fact of these composites. Koo et. al. and Zammarano et. al. [6, 7] has observed that CNF delays the fire time (Fire retardant property) hence, no dripping of CNF based thermoplastic materials. This phenomena may be understood as higher thermal conductivity of CNF than PTFE absorbs the more heat in composite system and transfer to polymer system; thus during heat transfer the polymer stick to CNF; this delays the fire action in terms of slow dripping of composite system. In general, the thermal conductivity of PTFE depends upon its crystallinity [8]. Since, the TGA of a substance enables to determine its mass as a function of temperature/time when the sample specimen is heated in chamber of controlled temperature and controlled ambient. Upon heating a sample specimen, its weight may increase or decrease. Before, proceed to explore the reason of increased mass we must have a tour to the technical sources of errors in reading the TGA mass. TGA measures are taken when sample specimen is heated or cooled in a system (chamber). The

effect of ambient can be observed by flowing an inert or a reactive gas (air or oxygen – oxidative TGA study). To hold the sample specimen, a sample pan is supported by a precision balance either above the balance via a stem /support rod or below the balance (hang-down). Gravity provides accurate and reproducible measurements. Whereas, thermal analysis with differential scanning calorimetry (DSC) is associated with the investigation of several phenomena occurring during the thermal heating when the heat is evolved or used as in a phase transition or in any chemical reactions. It is a widely used method for the investigation of the α -transition in polymers and their composites which is related to the Brownian motion of the main chains at the transition and relaxation of associated dipoles (glassy to the rubbery state) [9]. If calibration routines of TGA/DSC are correct then next possibility is the factors associated with cleaning process because deposition of impurities or foul gases may also cause the misleading interpretations.

EXPERIMENTAL:

The presented CNF/PTFE composite samples of circular shapes were fabricated by mixing of known weight of CNF (Aldrich Prod. No 719781) and PTFE (FP306010 from Goodfellow) by simple dispersive mixing method. More details can be found in our published work somewhere [10].

Thermal study:

DSC and TGA of composite sample 3, 7, 10 and 26 wt% of CNF were done on "Mettler Toledo (TGA/DSC1)". TGA study was done in air ambient at the rate of 10°C per minute.

RESULT AND DISCUSSION:

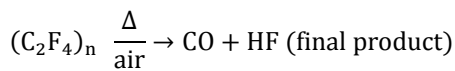
Fig.1 (a), (b), (c) and (d) are combined curves of TGA/DSC of samples 3, 7, 10 and 26 wt% of CNF respectively. In all samples shown below, the pattern of DSC curves remained

same. At 3 wt% (lower) of CNF in PTFE, the TGA curve of composite is a normal curve (Fig. (a)) with two steps. For 7 wt% of CNF, an increase in mass of composite is observed at very lower temperature (44°C) ($\Delta = 0.04\text{mg}$) (Fig. (b)). For higher weight percent increase in mass follows as 0.04mg for 7 wt%, 0.08mg for 10 wt% and 0.14mg for 26 wt%. However, the cooling curve is normal and same for three samples namely samples 3, 7 and 10wt% of CNF loading (Fig.1 (a), (b) and (c)) while the mass remained increased for sample 26wt% (Fig.1 (d)).

Explanation of Increased Mass of Composite with Temperature:

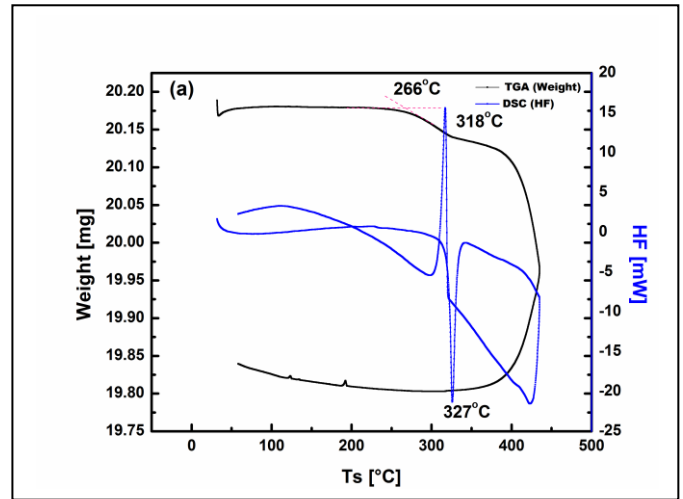
Few experimental parameters pertained to TGA systems have been blamed of the abnormal behavior of mass increase of polymer resins in TGA experiments [11]. Since cross linking density of epoxy based materials has direct relationship with temperature therefore, in polymer, a tendency of increased mass with temperature can be cross-linking due to thermal activation [12, 13]. Since PTFE is chemically inert therefore, it does not cross-linked like an elastomer but Teflon 100 FEP-fluorocarbon resin has been reported to cross-links when exposed at elevated temperatures to radiation [14]. However, in our case, the higher conductivity of CNF than PTFE might show its effect with PTFE at increased wt% of CNFs (i.e. 10 and 26 wt%) in composite. Hence, in air ambient, a chemical interaction might be the suspected reason of increased mass. Since, it is the tendency of heat flow that during flow of heat from higher (CNFs) to lower (PTFE) the two surfaces be in contact with each other. Then some chemically interactive [15] changes in proportion might take place at higher temperature by PTFE with the ratio of CNF loading.

However, one more clue adds more to thinking that, in air at 350°C, the exact decompose (degradation) mechanism of PTFE is found somewhere as [16].

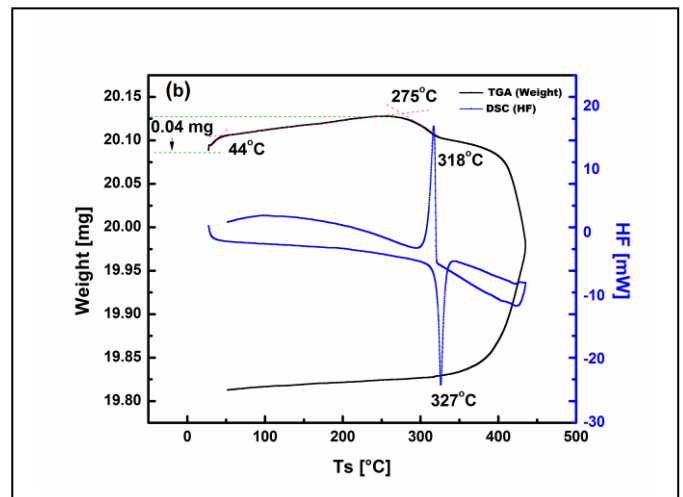


On the bases of above, one may also suspect slight increase in mass with increasing temperature because of trapped gas (released CO) within composite [16]. However, the cooling curve of sample (d) does not come to its initial original mass or to lesser value of its mass. In our case as mentioned that at higher temperatures, the CO gas is released in air ambient by PTFE. This released CO can contribute to increase the mass after heat treating the sample in chamber if carbon yield gets deposited on the pan after reduction of possible metal (Transition) oxides in the (Chamber) system. Hence, carbon yield can have contribution in increasing the mass of composite. Such reduction is observed during production of Vapor-Grown CNF (VGCNF) process by chemical vapor deposition (CVD) technique where CO is introduced in the

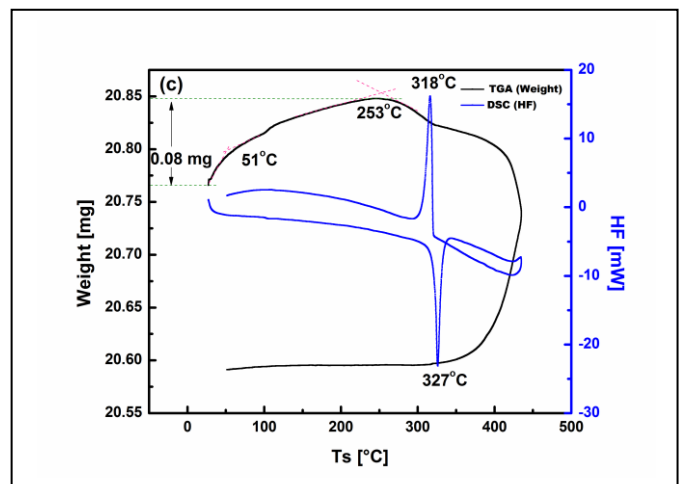
gas flow to increase the carbon yield through reduction of possible iron oxides in the system [17]. Therefore, we conclude that most supportive reason of increased mass of 26wt % sample is deposition of yielded carbon on the sample holder pan/sample.



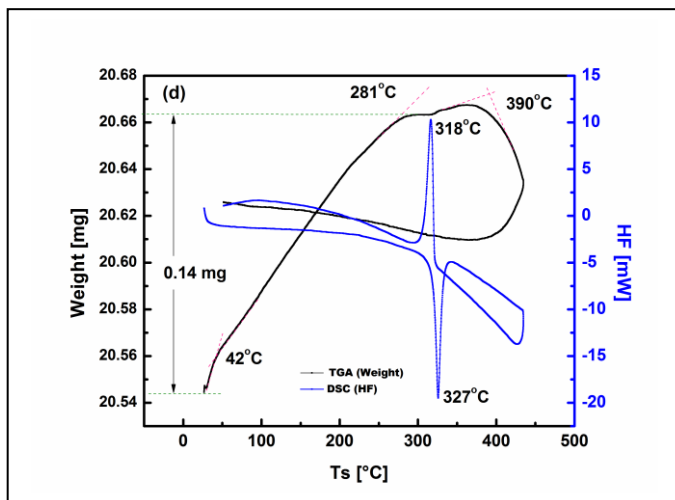
(a)



(b)



(c)



(d)

Figure 1 (a), (b), (c) and (d) are combined curves of TGA/DSC of samples 3, 7, 10 and 26 wt% of CNF.

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