Thermal degradation kinetic study of polypropylene co-polymer (PPCP) nanocomposites

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Abstract - *In the study, polymer nanocomposites were prepared by using polypropylene co-polymer (PPCP), maleic anhydride grafted polypropylene (MAgPP) and multiwall carbon nanotubes (MWCNTs). The thermal stability of the in-house prepared nanocomposites was studied using thermogravimetric analysis (TGA). From the TGA data, it was observed that the thermal stability of the nanocomposites increased significantly with the increase in MWCNTs loading in the nanocomposites. Thermal degradation kinetics was studied from the data obtained from TGA analysis. Coats-Redfern (CR) method was used to evaluate the thermal degradation kinetic parameters such as degradation reaction order, activation energy and frequency factor of the nanocomposites using TGA data. From the kinetic study results, it was observed that the thermal degradation process mostly followed 0.5 order. The estimated degradation activation energy of the nanocomposites was in the range of 120-355 kJ/mol. The observed activation energy was around 1.9 times higher in presence of 2 wt.% MWCNTs with respect to the nanocomposite without MWCNTs. From the study, it can be concluded that the MWCNTs offered better thermal properties to the nanocomposites.*

Key Words: Nanocomposites; MWCNTs; Thermal degradation; Kinetic study, Activation energy.

1. INTRODUCTION

In recent years, carbon nanotubes (CNTs) filled polypropylene co-polymer composites [1] have been considered as the most versatile and economic way to engineer a material with specific desired properties. Wide application of this polymer can be found in areas such as auto mobile, electronic, food packaging, textile, transportation and other industrial sectors. Polypropylene Co-polymer (PPCP) is polymer that has relatively good mechanical properties and low-cost. However, PPCP is also well-known for having low thermal stability or low heat distortion temperature. This shortcoming of PPCP makes its applications limited. For example, food container made from PPCP could not be used in oven or microwave at a relatively high temperature, electronic parts or semiconductors made from PPCP has small range of operating temperature, and PPCP coating in subsea pipelines could not withstand a relatively high crude oil temperature in a long intended lifetime.

Multiwall carbon nanotubes (MWCNTs) have been reinforced in the composites to improve the thermal stability. The carbon nanotubes have a tendency to form agglomerates during synthesis because of van der Waals attraction between nanotubes. In the composites, these agglomerations decrease the surface area and disturb the formation network structure which is essential to improve mechanical properties and the main task of processing is to dissolve such agglomerates as good as possible. Therefore, uniform dispersion of the nanotubes [2] is required to realize the potentiality of the nanotubes as reinforcing fillers. Common methods for the preparation of CNT filled polymer composites include in situ filling polymerization, solution mixing and melt blending. In situ polymerization and solution mixing techniques have many limitations, including that they may not be commercially viable and are environmentally contentious. Many properties such as electrical conductivity, mechanical strength and thermal stability are strongly affected by the network structure which can restrain the mobility of the polymer chains in polymer/CNT nanocomposites. The extent of property improvement in CNT filled polymer composites generally depends on several factors such as volume fraction of fillers, dispersion of CNTs in polymer matrix, type of polymer employed and fabrication method, etc.

The thermal degradation of polymers is a phenomenon where the polymeric material at elevated temperature undergoes chemical changes. The study of thermal degradation of polymers is important for developing an efficient technology for polymer processing and in understanding the thermal degradation mechanism. The study is also important in understanding their applicability at elevated temperature and storage [3]. Thermogravimetric analysis (TGA) is a useful technique to evaluate the thermal

decomposition behavior, melting, stability, and thermodynamic parameters of the polymers.

Chaudhary et al. [4], have studied the kinetic and thermodynamic parameters of various polymers by thermogravimetric method. In the study, Coats-Redfern method was used to estimate the kinetic parameters of various coordination polymers. The reported activation energy was in the range of 30-105 kJ/mol depending on types of polymer and for a reaction order of around 1.5. Burkanudeen et al. [5] have studied the thermal degradation kinetics of terpolymer resins. Freeman-Carroll and Sharp-Wentworth methods were used to estimate the kinetic parameters, such as, activation energy, order of reaction, entropy and free energy of activation. The reported activation energy and order of reaction were 24 kJ/mol and 0.92 respectively.

Vasconcelos et al. [6], have studied the decomposition kinetics of poly (ether-ether-ketone) polymer using TGA technique with multiple heating rates. Flynn-Wall-Ozawa and Coats-Redfern models were used to estimate the degradation activation energy. Fatemeh et al. [7] have studied the thermal degradation kinetics of bisphenol A (BPA)-based epoxy resin and lignin-based epoxy composites using TGA-FTIR analysis under non-isothermal condition. In the study, it is reported that lignin-based epoxy composites are more thermally stable and offered higher degradation activation energies in comparison with BPA-based epoxy resin.

Zhiming et al. [8] have studied the thermal degradation kinetics of polypropylene using TGA analysis. In the study, the reported degradation reaction order was 0.35, and the reported activation energies of the polymer was in the range of 125-140 kJ/mol. Qin et al. [9] have studied the thermal stability and thermal degradation kinetics of polypropylene (PP)/clay microcomposites and nanocomposites using thermogravimetric analysis (TGA) with the help of Kissinger method, Coats-Redfern method, and Freeman-Carroll method. In the study, it was reported that pure polypropylene followed first-order and the composites followed zero-order kinetics. The activation energy of the composites increased dramatically, and the reported activation energies are in the range of 110-570 kJ/mol.

Zhou et al. [10] have studied the effects of multi-walled carbon nanotubes (MWCNTs) size and loading on thermal properties and thermal stability of polypropylene (PP) composites using thermogravimetric analysis. In the study, it was reported that the decomposition temperature increased with increasing of filler loading and its length-to-diameter ratio. Rajesh Kumar et al. [11] have prepared the MWCNT/Maleic anhydride grafted polypropylene (MAgPP)/PP nanocomposites and estimated various properties such as thermo-mechanical (i.e., Vicat softening temperature (VST), heat deflection temperature (HDT)),

thermal (i.e., melting temperature, crystallization temperature and thermal degradation temperature), and electromagnetic interference (EMI) shielding properties. In the study, it was reported that the thermo-mechanical properties of the composites increased with the increase of MWCNTs loading.

From the literature, it is observed that most of the studies are available on the thermal degradation kinetics of various polymer based composites such as polypropylene, poly (ether-ether-ketone, epoxy etc. However, to the best of our knowledge, the literature pertaining to the thermal degradation kinetics of PPCP based nanocomposites in presence of MWCNT and MAgPP is not disclosed in the open literature. Therefore, the objective of the present study is to study the thermal degradation behaviour of the in-house prepared nanocomposites and estimation of its degradation kinetic parameters.

2. MATERIALS AND METHODS

2.1. Materials

Polypropylene co-polymer (melt flow index = 9 g/10 min at 230 °C) was purchased from Reliance Polymers (Mumbai, Maharashtra, India). The MWCNT-PP master batch contains 20 wt.% of MWCNT procured from Hyperion Catalysis International (Cambridge, USA). Maleic anhydride grafted polypropylene (melt flow index = 110 g/10 min at 190 °C) was procured from Plus Advanced Technologies Private Limited (Gurugram, Haryana, India).

2.2. Preparation of nanocomposites

The nanocomposite preparation process is shown in Figure 1. In the process, required amounts of pellets of PPCP, MWCNT-PP master batch along with MAgPP compatibilizer were added into the extruder. The extrusion process was carried out at a temperature of 190-230 °C; and mixed through the action of the two counter-rotating blades at a rotor speed of 80 rpm. After that, the extruded product was cut into pellets and dried at room temperature. Following that, the pellets were fed into an injection moulding machine (Japan Steel Works, India) that was operated at a temperature of 190-210 °C, speed of 100 rpm and holding pressure of 300 bar. For testing and characterization, the pellets were moulded into conventional shapes and cooled to room temperature. Table 1 shows the composition of the composites used in this study. A control sample, i.e., a polypropylene co-polymer along with MAgPP sample, was also prepared using a similar procedure.
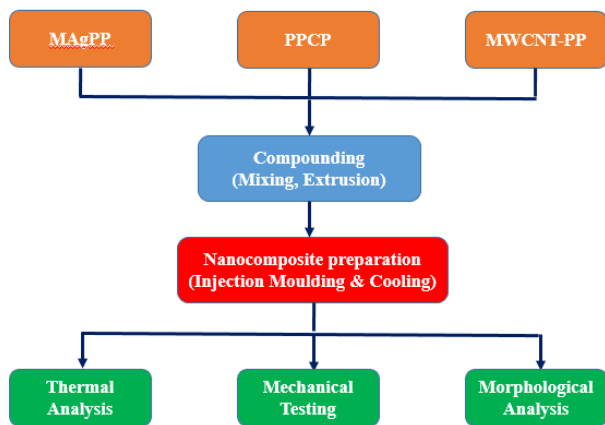
Figure 1. Flow chart of processing and characterization of PPCP/MAgPP/MWCNT Composites.
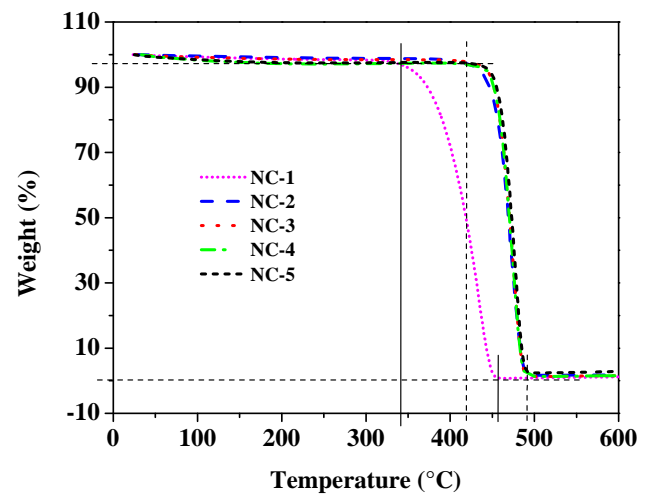
Table 1. The chemical composition of PPCP nanocomposites.

Sample No.	PPCP (wt.%)	MAgPP (wt.%)	MWCNT (wt.%)
NC-1	98.0	2.0	0.0
NC-2	97.5	2.0	0.5
NC-3	97.0	2.0	1.0
NC-4	96.5	2.0	1.5
NC-5	96.0	2.0	2.0

2.3. Characterization of the in-house prepared nanocomposites

The thermal stability and degradation behavior of the nanocomposites were estimated using the thermogravimetric analysis (TGA) (TGA/SDTA 851e Thermogravimetric analyzer, Mettler Toledo, Switzerland). The TGA measurements were recorded in the temperature range of 30-600 °C at a heating rate of 20 °C/min under the nitrogen environment.

3. RESULTS AND DISCUSSIONS

3.1. Thermogravimetric analysis of the in-house prepared nanocomposites

To study the thermal stability and degradation kinetics of the in-house prepared nanocomposite products, thermogravimetric analysis was carried out using a TGA instrument. The nanocomposite sample was taken in the sample pan and heated it from 30 °C to 600 °C at a heating rate of 20 °C/min under the nitrogen environment. The obtained TGA-thermograms of the nanocomposite samples are shown in Figure 2.

Figure 2. TGA thermograms of PPCP nanocomposites at different amounts of MWCNTs.

From the TGA thermograms, it is observed that the PPCP nanocomposite without MWCNT content (NC-1) is thermally stable up to a temperature of more than 300 °C with a mass loss of below 2 wt.%. However, the thermal stability of the nanocomposites increased significantly in presence of MWCNTs. The nanocomposites NC-2, NC-3, NC-4 and NC-5 are thermally stable up to a temperature of greater than 400 °C with a mass loss of below 2 wt%. It is also observed from the thermograms that all the materials are decomposed almost completely at around 500 °C with a residual mass of around 2 wt.%.

3.2. Thermal degradation kinetics of in-house prepared nanocomposites

Thermogravimetric techniques have been widely used to study the thermal degradation kinetics of polymer materials. Different methods, such as, Kissenger-Akahira-Sunoe (KAS) method, Flynn-Wall-Ozawa (FWO) method, Friedman method, Madhusudhanan-Krishnan-Ninan (MKN) method, and Coats-Redfern (CR) method have been proposed by many authors to estimate the kinetic parameters for thermal degradation of polymer materials. Among the various methods, CR and MKN methods are very popular to estimate the kinetic parameters from the weight loss data of materials for a fixed heating rate. In the present study, degradation kinetics of the in-house prepared nanocomposites are evaluated from the weight loss data obtained from the TGA thermograms under non-isothermal condition. The TGA data was coupled with Arrhenius equation to find the thermal degradation kinetics. Coats-Redfern method has been used to evaluate the kinetic parameters with the help of the data obtained from the TGA thermograms.

The logarithmic form of Arrhenius equation can be written as:

$$\log k = \log A - \frac{E}{2.303RT} \qquad (1)$$

where, k is degradation rate constant, T is temperature (K), A is frequency factor (1/s), R is gas constant, and E is activation energy.

The rate expression for a non-isothermal degradation reaction is expressed as:

$$\frac{dx}{dt} = A.e^{-E/RT}.f(x) \qquad (2)$$

where, x is the fractional conversion of a sample at time t.

The fractional conversion of the material at a particular temperature x_T was calculated using the following expression:

$$x_T = \left(\frac{W_i - W_T}{W_i - W_f}\right) \qquad (3)$$

where W_i, W_f and W_T are initial weight, final weight and weight at a particular temperature respectively. Final weight was considered based on the plateau region of a thermogram.

If $f(x) = (1-x)^n$ (where n is order of degradation reaction) and constant heating rate, $a = dT/dt$, then according to the Coats-Redfern method, the Arrhenius equation can be expressed by the following relations:

$$\log\left(\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right) = \log\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.303RT} \qquad \text{(for } n \neq 1)$$
$$(4)$$

$$\log\left(\frac{-\log(1-x)}{T^2}\right) = \log\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.303RT} \qquad \text{(for } n = 1)$$
$$(5)$$

$$Y = -\log\left(\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right) \qquad \text{(for } n \neq 1) \qquad (6)$$

$$Y = -\log\left(\frac{-\log(1-x)}{T^2}\right) \qquad \text{(for } n=1) \qquad (7)$$

The order of degradation kinetics was estimated by setting different values of 'n' in Eq. (6) or Eq. (7). The values of 'Y' were estimated from the TGA data and plotted against the

reciprocal of degradation temperature. The Coats-Redfern plots were drawn for the in-house prepared nanocomposites for different values of 'n' and the corresponding plots are shown in Figure 3. From Figure 3, it is noticed that the thermal degradation of nanocomposites followed mostly 0.5 order. The values of activation energy (E) and pre-exponential factor (A) were calculated from the slope *(–E/2.303R)* and intercept *log[(AR/aE)(1–(2RT/E)]* of linear equation for the best fit curve (higher R^2 value). The estimated values of degradation reaction order, activation energy and pre-exponential factor obtained from the Coats-Redfern plots are tabulated in Table 2.
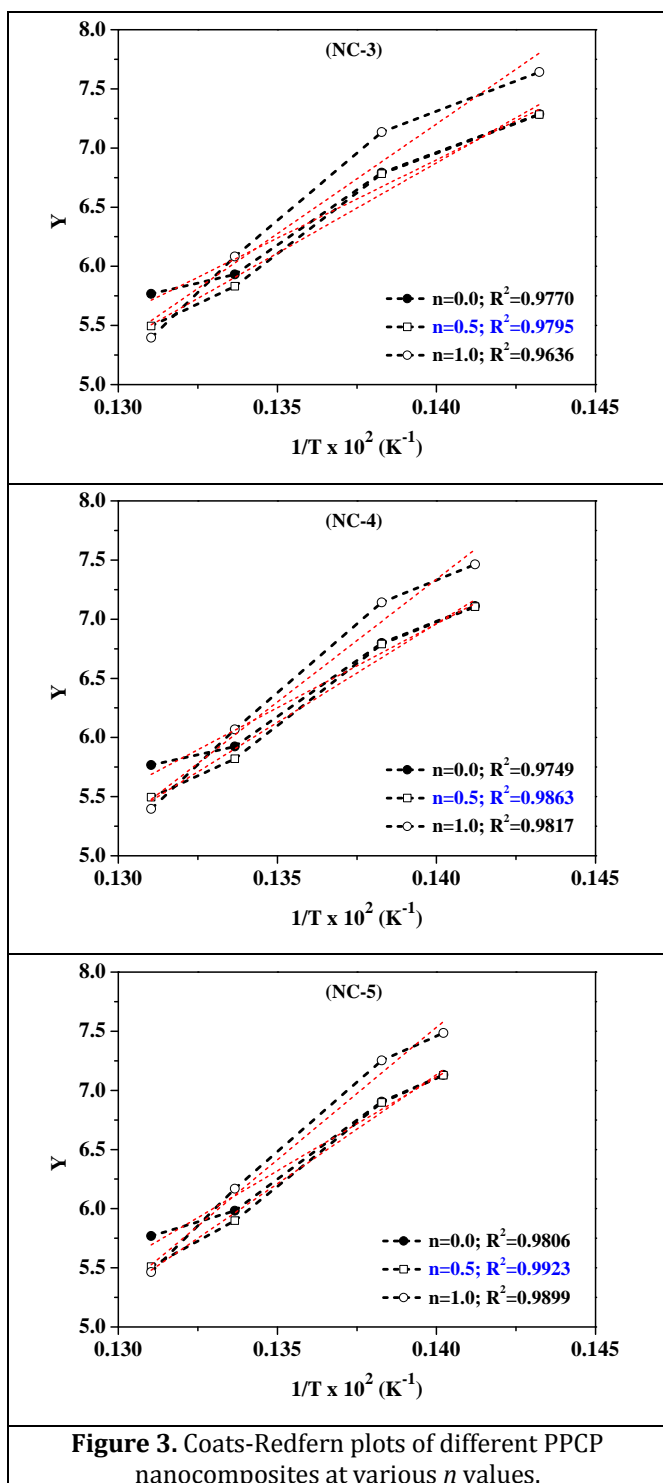
Figure 3. Coats-Redfern plots of different PPCP nanocomposites at various *n* values.
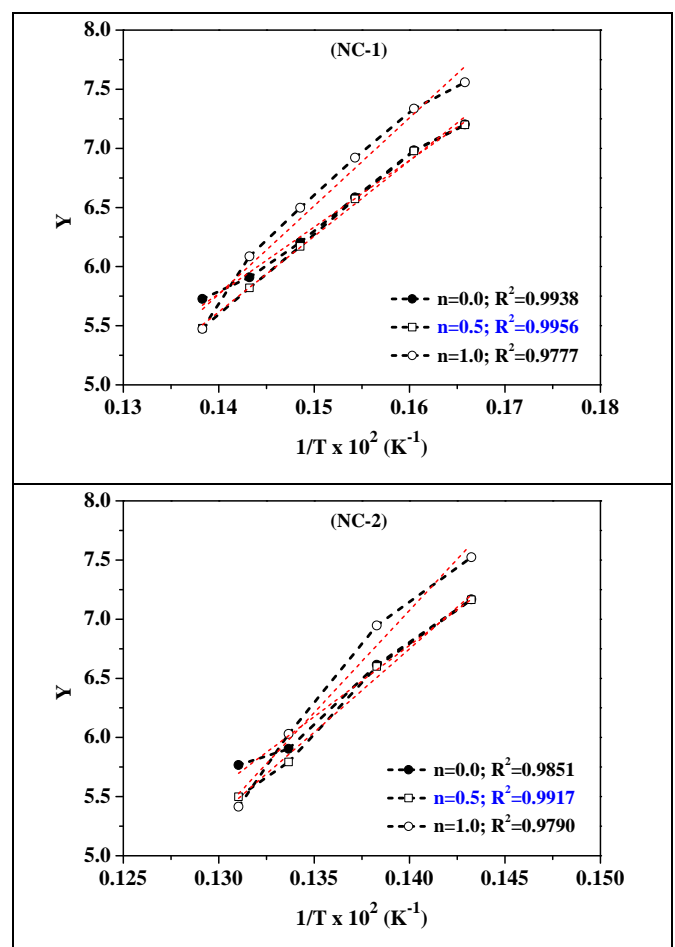
Table 2. Kinetic parameter values of different nanocomposite products.

Sample No.	Order, n	R^2 value	E (kJ/mol)	A (1/s)
NC-1	0.5	0.9956	122.43	2.5094
NC-2	0.5	0.9917	269.91	1.1687×10^{-9}
NC-3	0.5	0.9795	292.41	3.8102×10^{-11}
NC-4	0.5	0.9863	319.81	5.0491×10^{-13}
NC-5	0.5	0.9923	352.90	3.1214×10^{-15}

From the data (Table 2), it is observed that the thermal degradation reaction of in-house prepared nanocomposites followed around 0.5 order. Further it is observed from the data that the activation energy of the in-house prepared nanocomposite in presence of MWCNTs (NC-2) is more than double with respect to the nanocomposite in absence of MWCNTs (NC-1). The observed activation energy is around 1.9 times higher in presence of 2 wt.% MWCNTs with respect to the nanocomposite without MWCNTs. The increase in activation energy with the addition of MWCNTs indicates that the thermal stability of the nanocomposites increased in presence of MWCNTs. The decrease in frequency factor values indicates that the rate of thermal degradation is slowed down with the increase of MWCNTs loading in the nanocomposites i.e., with the increase of thermal stability of the nanocomposites. In the study, the estimated activation energy of the in-house prepared nanocomposites is in the range of 120-355 kJ/mol for a 0.5 order degradation reaction.

4. CONCLUSIONS

In the study, polymer nanocomposites were prepared by using polypropylene co-polymer (PPCP), maleic anhydride grafted polypropylene (MAgPP) and multiwall carbon nanotubes (MWCNTs). The thermal stability of the in-house prepared nanocomposites was studied using thermogravimetric analysis (TGA). From the TGA data, it was observed that the thermal stability of the nanocomposites increased significantly with the increase in MWCNTs loading in the nanocomposites. Thermal degradation kinetics was studied from the data obtained from TGA analysis. Coats-Redfern (CR) method was used to evaluate the thermal degradation kinetic parameters such as degradation reaction order, activation energy and frequency factor of the nanocomposites using TGA data. From the kinetic study results, it was observed that the thermal degradation process mostly followed 0.5 order. The estimated degradation activation energy of the nanocomposites was in the range of 120-355 kJ/mol. The observed activation energy was around 1.9 times higher in presence of 2 wt.% MWCNTs with respect to the nanocomposite without MWCNTs. From the study, it can be concluded that the MWCNTs offered better thermal properties to the nanocomposites.

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