Reaction model to predict the thermal degradation mechanism of polypropylene – carbon nanotube composite

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ARTICLE INFO

Article History:
Received: 27-08-2020
Revised: 25-09-2020
Accepted: 27-09-2020

Keywords:
Polypropylene; CNT composite; Degradation; PP/MWCNT

How To Cite:
Alauddin, Khan, A., Ahmed, I. (2020). Reaction model to predict the thermal degradation mechanism of polypropylene – carbon nanotube composite. Indonesian Physical Review, 3(3), 111-123

DOI:
https://doi.org/10.29303/ipr.v3i3.62

ABSTRACT

The degradation of polymer is known, but the effect of CNT composite is the less studied concept. In this article, the effect of CNT on degradation is presented. The first stage involved a literature study for reaction mechanisms in oxidative thermal degradation of Polypropylene (PP). A reaction model is then developed by considering mass balance on various reactive species. Literature is reviewed to find or estimate the model parameters. The parameters not found in the literature are fitted. The model equations are solved after assuming initial conditions and values of various parameters. After the PP polymer degradation modeling comparison drawn between PP and PP/MWCNT composite by making a hypothesis based on Arrhenius equations (activation energy increases, the rate constant decreases, and therefore the rate of reaction decreases). The result shows that the CNT composite takes much time to degrade as compared to the polymer.

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Introduction

Recently the use of carbon nanotube-polymer composites as mechanical enhancements and also as electronic devices has been realized [1]. For example, the composites exhibit a higher energy storage capacity, compression modulus, and can be used as a field emission source and in optoelectronic and electromagnetic devices. However, the incorporated carbon nanotubes physical and chemical influence on the polymers has not been widely studied. Polypropylene is a material of high economic importance, which is susceptible to oxidative degradation under a variety of environmental factors. During the past four decades, many excellent studies have contributed to the difficult goal of building an understanding of the exceedingly complex mechanisms that underlie polypropylene degradation. In this, there is an overview of polypropylene thermal degradation and, after that, the effect of CNT on the thermal degradation of polypropylene CNT composite [1,2].
Reaction Mechanism on Thermal Degradation of Polypropylene

In this section, thermal degradation of PP in which basic chemical reactions of free radical initiation, oxidation, propagation, termination, and stabilization are considered to predict the time span of various free radical species and antioxidants by reaction model.

Thermal Oxidative Degradation of Polypropylene

The long-term thermal degradation of PP is due to an auto-oxidative process [3,4]. Autooxidation occurs in the open air or in the presence of oxygen and forms peroxide and hydroperoxide. In many publications, this auto-oxidative process is described by the mechanism known for the auto-oxidation of low molecular weight hydrocarbons. Bolland and Gee [5] were the first to apply auto-oxidation to degrade the polymer. In 1946, they used this mechanism to describe the oxidation of rubber. Since then, this mechanism has also been applied successfully to other polymers such as polypropylene (PP). It is shown that PP in an environment without oxygen does not degrade significantly [5,6]. Therefore oxidative degradation is considered as the main cause of degradation. Oxidative degradation begins with an initiation step, which generates alkyl free radicals. These free radicals then get oxidized and react through propagation, chain scission, termination, and stabilization reactions. Some of these reactions are fast, some are slow, while some others are insignificant in "AO protected" timespan during which AO is still active in protecting the polymer.

Initiation

In thermal degradation, initiation is primarily due to cleavage of weak C-C bonds that occurs during polymer processing in PP molecule where bond-dissociation energy (BDE) in between secondary carbon and tertiary carbon [C-C] is 81.6 kcal mol⁻¹ [7]. In thermal degradation, the breakage of C-C bond can be caused by energy input from heat which generates highly reactive and unstable alkyl free radicals (·R) on PP molecule.

Among all the different types of bonds possible in a PP molecule, the bond between secondary carbon and tertiary carbon is found to be the weakest (whose BDE is less than 81.6 kcal mol⁻¹). Therefore it is expected that it breaks first in a PP molecule during aging. This initiation reaction is represented by reaction refer to (1) (corresponds to reaction R.i in Table 2. Here, a monomeric unit in PP molecule is considered as RH group, two RH group which generate two alkyl free radicals (represented as 2·R)

\[
2RH \rightarrow 2\cdot R
\]

(1)

Propagation

In thermal degradation, the propagation reaction starts from the oxidation of alkyl free radical, which generates peroxide radical as given by the reaction in reaction refer to (2).
$\sim \text{CH}_2-^\circ \text{C} \sim + \text{O}_2 \rightarrow \sim \text{CH}_2-^\circ \text{C} \sim$

$R + \text{O}_2 \rightarrow \text{ROO}$ (2)

**Table 1.** Bond dissociation energy of various molecule which may be considered for initiation

| Molecule     | Location | BDE(kcal mol$^{-1}$) | Reference |
|--------------|----------|-----------------------|-----------|
| Ethane       |          | 101.1                 | [8]       |
| Propane      |          | 98.6                  | [8]       |
| n-Butane     |          | 98.2                  | [8]       |
| iso-Butane   |          | 96.5                  | [8]       |
| iso-Octane   |          | 84.1                  | [8]       |
| iso-Heptane  |          | 81.6                  | [8]       |

The peroxide radical ROO$^\cdot$, abstract hydrogen from PP molecule and generates hydroperoxide group, ROOH, and an alkyl radical as shown in reaction refer to (3), (Corresponding to R.1 in table 2)
The hydroperoxide group, ROOH, is relatively stable, yet can slowly decompose. The decomposition of hydroperoxide can be described by several mechanisms [9,10,11]. In the most common mechanism, two adjacent hydroperoxides can decompose according to reaction refer to (4), below (corresponding to R.3 in table 2), which has lower activation energy than the unimolecular decomposition given by reaction refer to (5) [12]. (Corresponding to R.3 in Table 2)

\[
2\text{ROOH} \rightarrow \text{RO}^\cdot + \text{RO}^\cdot + \text{H}_2\text{O} \quad (4)
\]

Mechanical properties deteriorate because of chain scission. This can occur due to rearrangement on a PP molecule due to free-radical presence, causing the scission of the C-C bond at the beta position. Among the oxide and peroxide radicals, RO radical is less stable than ROOH radical. Therefore, polymer chain scission can occur via rearrangement by β-scission of an oxide radical (RO) on secondary or tertiary carbon as shown in reaction refer to (5), (Corresponding to R.4 in Table 2).

\[
\text{RO}^\cdot \rightarrow \text{R}^\cdot + \text{RO}^\cdot \quad (5)
\]
Termination reactions are bimolecular reactions between two free radicals that are in close proximity giving stable products. These termination reactions decrease the concentration of free radicals responsible for the propagation of the degradation reactions.

In reaction, refer to (6), which two peroxide radical (ROȮ) react to form inert product (ROOR) and release oxygen. (Corresponding to R.5 in Table 2)

$$2ROȮ \rightarrow O_2 + ROOR$$  \hspace{1cm} (6)

Stabilization

An effective way to inhibit PP degradation by free radicals is to stabilize them with phenolic AOs. The rate constants of AO stabilization reactions are significantly greater than the rate constants of free radicals reacting with alkyl groups in PP. Also, the concentration of phenolic groups in AO, [AOH] is usually much higher than free radicals, therefore as long as AOH is available, stabilization dominants over propagation hence preventing polymer degradation. This AOH rich period corresponds to the AO protected timespan used in this study.

Reactions show the main stabilization reactions involving AOs refer to (1) and (8) (corresponding to R.6 and R.7 in Table 2) where, AOH represents a phenolic group on an antioxidant molecule, and AȮ represents a phenoxy group than has donated an electron in the process of stabilizing a free radical

$$ROȮ + AOH \rightarrow ROOH + AȮ$$  \hspace{1cm} (7)
The molecular structure of phenolic antioxidant, which is considered in this [Irganox-1076] is a mononuclear phenol which has a linear chain hydrocarbon molecule with a phenolic head and is capable of stabilizing one free-radical

\[
R\dot{O} + AOH \rightarrow ROH + A\dot{O}
\]  

(8)

In reactions refer to (7) and (8), one phenolic group (AOH) stabilizes one free radical, and their reaction constants are expected to be the order of 10^6 cm^3 mol^-1 s^-1 under the conditions of thermal aging at around 85°C

| RN | Reaction | Category | Description | Significance |
|----|----------|----------|-------------|--------------|
| Ri | RH → Ṙ | Initiation | C-C scission | Insignificant |
| R1 | Ṙ + O₂ → ROȮ + Ṙ | Propagation | Peroxide radical formation | Fast |
| R2 | RO+ RH → ROOH | Propagation | Hydroperoxide group formation | Slow in the presence of AOH |
| R3 | ROOH + RH → ṘO + Ṙ + H₂O | Propagation | Decomposition of Hydroperoxide | Slow at low concentration of ROOH |
| R4 | ṘO → R=O + Ṙ | Propagation | Depolymerization by β scission | Fast |
| R5 | 2ROȮ → O₂ + ROOR | Termination | Termination by combination | Very slow |
| R6 | ROȮ + AOH → ROOH + A\dot{O} | Stabilization | Stabilization of Peroxide Radical | Fast |
| R7 | ṘO + AOH → ROH + A\dot{O} | Stabilization | Stabilization of oxide Radical | Fast |

Assumptions related to the Reactions

1. Ignore diffusion and physical loss of antioxidant and other reactive species, so that the concentration of all species depends on chemical reaction only.
2. Ignore the diffusion of oxygen.
3. All reactive species are immobile and uniformly distributed throughout the depth of the sample.
4. All reactions are first order in each reactant.
5. Reaction R.i requires high temperature. Therefore, under the low-temperature condition (85°C), it is insignificant and can be neglected.
6. The oxygen concentration dissolved inside the polymer is constant.
7. All reactions are elementary reactions.
8. PP sample contains some initial concentration of free radicals.

**Nomenclature**

| Symbol | Definition                      |
|--------|---------------------------------|
| R ·    | Free radical                    |
| RH     | Alkyl group                      |
| ROO·   | Peroxide radical                |
| RO·    | Alkoxide radical                |
| ROOH   | Hydroperoxide                    |
| AOH    | Antioxidant                      |
| AO·    | Antioxidant molecule that has donated one electron |

**Reaction Parameter**

Below is the rate constants (K), which are inferred from the literature for our degradation reaction.

\[
K_1 = 3.0 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ At } 80^\circ\text{C} \ [9] \\
K_2 = 1.0 \text{ cm}^3 \text{ mol}^{-1} \text{ At } 130^\circ\text{C} \ [7] \\
K_3 = 1.0 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1} \text{ At } 80^\circ\text{C} \ [9]
\]

The rate constant \( K_4, K_5, K_6, \) and \( K_7 \) are not found in the literature. Therefore, assumed values of these rates constant are (based on reaction speed),

\[
K_4 = 1 \text{ s}^{-1} \\
K_5 = 10^7 \text{ cm}^3 \text{ mol}^{-1} \\
K_6 = 10^6 \text{ cm}^3 \text{ mol}^{-1} \\
K_7 = 10^6 \text{ cm}^3 \text{ mol}^{-1}
\]

**Material Balance**

The general form of Material Balance Equation can be written as:

\[ \text{In} - \text{Out} + \text{Generation} = \text{Accumulation} \]

Since there is no in and out the term, so our material balance equation becomes

\[ \text{Generation} = \text{Accumulation} \]

**A material balance on \( \dot{R} \)**

Reactions R.1, R.2, R.3, and R.4 are responsible for the generation of alkyl free radicals. The overall material balance on \( \dot{R} \) gives
\[
\frac{d[\mathcal{R}]}{dt} = -K_1[\mathcal{R}][O_2] + K_2[R\mathfrak{O}][RH] + K_3[ROOH][RH] + K_4[R\mathfrak{O}]
\]

A material balance on RO\mathfrak{O}

Reactions R.1, R.2, R.5, and R.6 are responsible for generating peroxide-free radicals [RO\mathfrak{O}]. The overall material balance on RO\mathfrak{O} gives

\[
\frac{d[RO\mathfrak{O}]}{dt} = K_1[\mathcal{R}][O_2] - K_2[RO\mathfrak{O}][RH] - 2K_5[RO\mathfrak{O}]^2 - K_6[RO\mathfrak{O}][AOH]
\]

A material balance on RH

Reactions R.2 and R.3 are responsible for changes in the concentration of the alkyl group [RH]. The overall balance on RH gives

\[
\frac{d[RH]}{dt} = -K_2[RO\mathfrak{O}][RH] - K_3[ROOH][RH]
\]

A material balance on ROOH

Reactions R.2, R.3, and R.6 are responsible for changes in concentration of hydroperoxides [ROOH]. The overall balance on ROOH gives

\[
\frac{d[ROOH]}{dt} = K_2[RO\mathfrak{O}][RH] - K_3[ROOH][RH] + K_6[RO\mathfrak{O}][AOH]
\]

A material balance on R\mathfrak{O}

Reactions R.3, R.4, and R.7 are responsible for changes in the concentration of alkoxide radicals [R\mathfrak{O}]. The overall balance on R\mathfrak{O} gives

\[
\frac{d[R\mathfrak{O}]}{dt} = K_3[ROOH][RH] - K_4[R\mathfrak{O}] - K_7[R\mathfrak{O}][AOH]
\]

Material balance for AOH

It can be seen that antioxidant groups (AOH) are consumed mainly by reaction with alkyl-peroxide and alkoxide free radicals as in reactions R.6 and R.7. The overall mass balance on [AOH] gives

\[
\frac{d[AOH]}{dt} = -K_6[RO\mathfrak{O}][AOH] - K_7[R\mathfrak{O}][AOH]
\]

The oxygen uptake can be predicted in which reaction R.1 and R.5 can participate in the consumption generation of oxygen. In this model, the initial concentration of oxygen is considered to be \(10^6\) mol cm\(^3\)

\[
\frac{d[O_2]}{dt} = -K_1[\mathcal{R}][O_2] - 2K_5[RO\mathfrak{O}]
\]

Determination of initial concentration

In the above section, the Ordinary differential equation (ODE) system obtain, and for the solution of that require Initial Conditions for each species.

Concentration of oxygen

It is assumed that the concentration of oxygen dissolved inside the polymer is constant. This is because the amount of oxygen reacted due to slow degradation can be replenished by the absorption of oxygen from the surrounding atmosphere maintaining its concentration at saturation at all times.
Initial concentration of \( O_2 \)

Initiation reaction \( R.i \) may be assumed to occur only during melt processing at high temperatures and not during the usage or inventory storage. Therefore, it is assumed that the processed PE has some initial concentration of \( R \cdot \) and not generated during storage and usage by reaction \( R.i \).

\[
[O_2]_{sat} = 1.46 \times 10^{-6} \text{ mol cm}^{-3}
\]  

(9)

Initial concentration of \( R \)

At \( t = 0 \),

\[
[R] = [R]_0 = 10^{-14} \text{ mol cm}^{-3}
\]  

(10)

The initial concentration of \( RO \), \( RO \cdot \) and \( ROOH \)

It is assumed the initial concentration of these species is zero.

\[
[RO \cdot ]_0 = 0
\]  

(11)

\[
[R \cdot ]_0 = 0
\]  

(12)

\[
[ROOH]_0 = 0
\]  

(13)

Initial concentration of \( RH \)

\( RH \) is a monomeric polymer unit of PE with a molecular weight of 42.08 g mol\(^{-1}\). We can find the initial concentration of \( RH \) with the help of density.

\[
\text{Concentration} = \frac{\text{Density}}{\text{molecular weight}}
\]

\( PP \) has a density of 0.946 g cm\(^{-3}\)

\[
[RH]_0 = \frac{0.946 \text{ g cm}^{-3}}{42.08 \text{ g mol}^{-1}}
\]  

(14)

\[
[RH]_0 = 0.0224 \text{ mol cm}^{-3}
\]  

(15)

Initial concentration of antioxidant

Antioxidant concentration may be assumed to be 0.1 wt. %.

The molecular weight of Antioxidant (Irganox-1076) is 530.87 g mol\(^{-1}\).

\[
[AOH]_0 = \frac{0.1 \text{ g AOH}}{100 \text{ g of } PP} \times \frac{0.946 \text{ g cm}^{-3}}{530.87 \text{ g mol}^{-1}}
\]

\[
[AOH]_0 = 7.13 \times 10^{-6} \text{ mol cm}^{-3}
\]  

(16)

Polypropylene MWCNT based Composite Thermal Degradation.

Results: It is now well accepted that polymer–CNT composites' improved thermal stability are due to the following: barrier effect, the thermal conductivity of CNTs, physical or chemical adsorption, radical scavenging action, and polymer–nanotube interaction [10].
Barrier effect
The nanotube barrier effect of polymer–CNT composite degradation processes is mainly a mass transport barrier, which slows the escape of the volatile products during the process of degradation and the permeation of O2 or air. It is related to the network structure and dispersion of nanotube in the composites and the compact char formation. The well-dispersed nanotubes could hinder the transport of polymer degradation products from the condensed phase to the gas phase compared to composites with poorly-dispersed nanotubes [10].

Thermal conductivity of CNTs
It is well known that CNTs, as compared to the polymers, show higher thermal conductivity in the axial direction. The addition of CNTs will help conduct heat from the surface and facilitate heat dissipation within the composites, resulting in the slow degradation of the composites.

Effect of CNT on the activation energy of the PP/MWCNT compare to the PP.
Thermogravimetric Analysis of several studies[2, 13, 14] found that there is an increase in activation energy of the PP/MWCNT as compared to the PP. This can be used for modeling purposes. The TGA analysis [2] shows that the reaction which involves in the decomposition is somehow similar to some degradation reaction. So the reaction is similar to main-chain scission and cross-linking [11].

Consideration for Modeling
The Arrhenius equations relate the rate of a chemical reaction to the magnitude of the activation energy:

\[ k = A e^{-E_a/RT} \]  \hspace{1cm} (17)

Where Refer to (17),
Ea = activation energy
k = reaction rate coefficient or constant
A = frequency factor of the reaction. It is determined experimentally.
R = Universal Gas constant
T = temperature in Kelvin

The Arrhenius equation allows us to calculate activation energies if the rate constant is known, or vice versa. As well, it mathematically expresses the relationships we established earlier: as activation energy term Ea increases, the rate constant k decreases, and therefore the rate of reaction decreases.

For modeling purposes, a slight decrease in constant rate values for the effected reaction of pure PP because CNT’s presence does not affect the main degradation reactions in a composite[12]. After the alteration observation of outcome analyzed.

Result and Discussion
The observation is based on the Reaction model of PP and the PP/MWCNT, and here we can observe various things. The first observation is that the degradation of CNT composite
taking more time as compared to the polymer. The CNT does not directly participate in reaction but had a direct impact on the degradation reaction. So the composite takes much more time to degrade. The benefits of introducing the CNT in the polymer are huge, but it affects the polymer's degradation mechanism as polymer takes much high time to degrade. After the addition of CNT, it further takes more time to degrade. This can affect the ecosystem directly or indirectly.

Figure (1) shows various modeling outputs. The output signifies the effect of an increase in activation energy. The various radical concentration varies with time. The graph shows these concentration variation, (a) RH concentration variation, (b) \( \dot{R} \) concentration variation, (c) ROOH concentration variation, (d) RO\( \dot{O} \) concentration variation, (e) R\( \dot{O} \) concentration variation, (f) AOH concentration variation, (g) A\( \dot{O} \) concentration variation, (h) Oxygen uptake. The concentration of RH is constant up-to \( 3.2 \times 10^7 \) sec after that start decreasing. The decrease in pure PP is taking less time as compared to PP/MWCNT. For \( \dot{R} \), RO\( \dot{O} \), ROOH, and R\( \dot{O} \), the peak is at \( 2.8 \times 10^7 \) sec. The AOH to follow an approximately exponential decrease. As AOH decreases, the concentration of ROO\( \dot{O} \) increases. The concentration of A\( \dot{O} \) increases with time. This is because of all the AOH participating in stabilization reactions.

![Figure 1](image1.png)

**Figure 1.** Modeling graphs of composite (a) RH concentration variation, (b) \( \dot{R} \) concentration variation, (c) ROOH concentration variation, (d) RO\( \dot{O} \) concentration variation, (e) R\( \dot{O} \) concentration variation, (f) AOH concentration variation, (g) A\( \dot{O} \) concentration variation, (h) Oxygen uptake

**Conclusion**

Degradation is a widely studied topic around the world. New research is being carried out to enhance the polymer properties, and nanomaterials are also widely used for research. But the degradation effect of nanomaterial composite is less focused. In this article, the reaction model to predict the thermal degradation mechanism of polypropylene–carbon nanotube composite is presented. It is a theoretical concept that is present here, but it gives a broad overview. As activation energy increases, the rate of reaction decreases. This is the main concept that is used in modeling. The thermogravimetric analysis shows a significant increase in the activation energy of composite. As a result, the rate constant will also
decrease based on the Arrhenius equation relation. The modeling output also verified the increase in reaction time. The effect of CNT on degradation reaction is observed in the modeling. The increase in degradation time has advantages and disadvantages.

Acknowledgment

We acknowledge the support of our department (Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia). We give special thanks to Iftekhar Ahmad (Assistant Professor Department of Petroleum Studies, Z H College of Engineering and Technology, Aligarh Muslim University, Aligarh) for validating the reaction model.

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