Radiation Physics and Chemistry 136 (2017) 1–8

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Thermal degradation kinetics and estimation of lifetime of radiation grafted polypropylene films

Dev K. Mandal[a], Haripada Bhunia[a,*], Pramod K. Bajpai[a], Vinod Kumar Bhalla[b]

[a] Department of Chemical Engineering, Thapar University, Patiala 147004, Punjab, India
[b] Department of Computer Science and Engineering, Thapar University, Patiala 147004, Punjab, India

ARTICLE INFO

Keywords:
Polypropylene
Acrylic acid
Radiation grafting
Thermal kinetics
Lifetime estimation

ABSTRACT

In this research work, thermal stability and degradation behavior of acrylic acid grafted polypropylene (PP-*g*-PAAc) films were investigated by using thermogravimetric (TGA) analysis at four different heating rates 5, 10, 15 and 20 °C/min over a temperature range of 40–550 °C in nitrogen atmosphere. The kinetic parameters namely activation energy (E_a), reaction order (n) and frequency factor (Z) were calculated by three multiple heating rate methods. The thermal stability of PP-*g*-PAAc films is found to decrease with increase in degree of grafting. The TGA data and thermal kinetic parameters were also used to predict the lifetime of grafted PP films. The estimated lifetime of neat PP as well as grafted PP decreased with increase in temperature by all the three methods. Studies also indicated that E_a and lifetime of PP-*g*-PAAc films decreased with increase in degree of grafting, which may also be helpful in biodegradation of grafted PP films.

1. Introduction

Polypropylene (PP) is one of the most extensively used plastic materials in flexible packaging application due to its low cost, recalcitrant nature, chemical resistance, effective water and gas barrier properties (Briassoulis et al., 2004). PP is a petroleum derived product, highly stable and takes long time for degradation. High molecular weight synthetic polypropylene containing largely carbon-carbon bond are generally resistance to biodegradation due to microbes are not accessible to them because their hydrophobic in nature. After use, packaging films are dumped in open sites or different landfills, which produce huge waste management problem. Incineration and burning of packaging films is associated with serious health hazards. The waste management problem should be reduced by production of less harmful packaging materials.

Biodegradable packaging films provide an excellent solution for waste management problem. These films can be easily biodegraded into small byproducts and microorganisms will consume it as an energy source. In the degradation process, plastics are reduced to low molecular weight products due to the environmental effects such as heat, sunlight, etc. and latter they are utilized by microorganisms as carbon source. Degradable packaging films are produced by blending of two or more polymers such as linear low density polyethylene (LLDPE) (Singh et al., 2012a, 2011, 2012b), high density polyethylene (HDPE) (Madhu et al., 2014), and polypropylene (PP) (Choudhary et al., 2011; Jain et al., 2015, 2014; Ying-Chen et al., 2010) with poly lactic acid (PLA).

PP films are hydrophobic in nature due to lack of chemical functionalities and non-polarity. These drawbacks can be removed by inserting functionality to the backbone with hydrophilic monomers through grafting. Grafting polymerization is a well-known method for the modification of chemical and physical properties of polymeric materials (Chaudhari et al., 2012). Polymeric materials with high functionality can be achieved by the introduction of ions or components that enhance the hydrophilicity of grafted polymers. Grafting copolymerization can be achieved using several methods namely photoradiation, thermal, enzymatic, chemical and gamma-radiation grafting (Mandal et al., 2016). Among these methods, gamma-radiation grafting has particular advantage due to its extensive penetration in the polymer matrix and rapid radical production to initiate the grafting polymerization. From our previous work (Mandal et al., 2016), it was found that the biodegradability of acrylic acid grafted PP did not significantly improve beyond 35% degree of grafting due to cross-linking on the surface. Now, there is a need to know the thermal stability and lifetime estimation of different degrees of grafted PP films with the help of thermal degradation kinetics parameters.

TGA method is an excellent way to study the thermal degradation kinetics. It provides information on activation energy (E_a), reaction order (n) and frequency factor (Z) by using various kinetic models such as (Friedman, 1964), (Kissinger, 1957), (Flynn and Wall, 1966), (Paik

* Corresponding author.
E-mail address: hbhunia@thapar.edu (H. Bhunia).

http://dx.doi.org/10.1016/j.radphyschem.2017.03.036
Received 6 December 2016; Received in revised form 4 March 2017; Accepted 21 March 2017
Available online 22 March 2017
0969-806X/

Table 1
Conditions for preparing grafted PP films (of different degrees of grafting).

Polymer	Acrylic acid concentration (wt%)	Radiation dose (kGy)	Inhibitor concentration (M)	Solvent concentration (M)	Degree of grafting (wt%)
PP	–	–	–	–	–
PP18	8	8	0.12	0.2	18
PP26	12	12	0.09	0.1	26
PP35	16	8	0.06	0.2	35

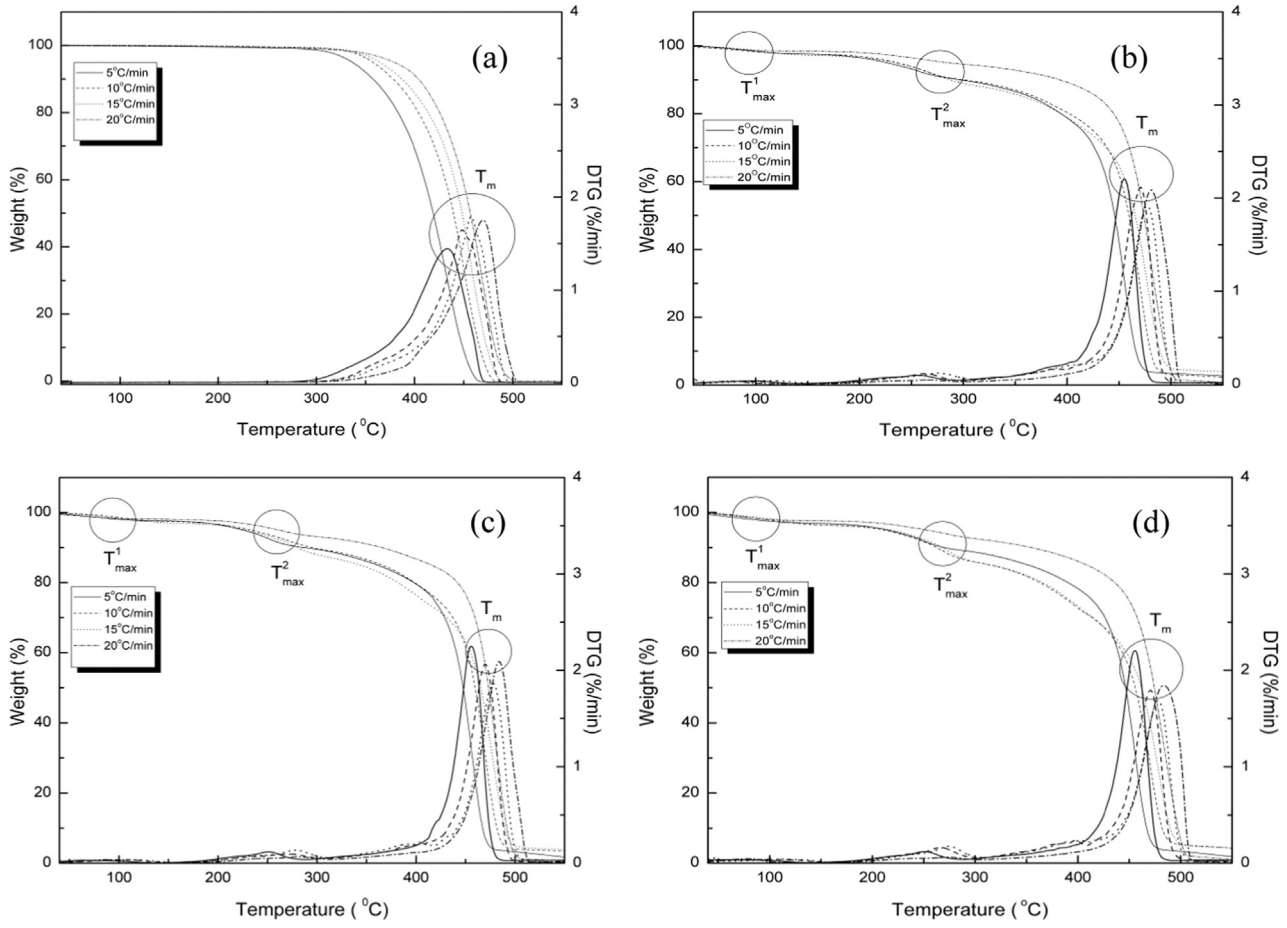

Fig. 1. TG and DTG curves of (a) PP, (b) PP18, (c) PP26, and (d) PP35.

and Kar, 2008) and (Madhu et al., 2016). The kinetic parameters obtained from these kinetic models can be used to calculate the lifetime of polymers at various temperatures. Madhu et al. (2016) studied the thermal degradation kinetics and lifetime of HDPE/PLA/pro-oxidant blend and found that the lifetime of HDPE decreases with increase in the concentration of cobalt stearate (CoSt). Thermal degradation and lifetime of the film samples depends not only on the fractions of their constituents, but also on calculation methods and heating rates. Chen and Wang (2007) studied the thermal degradation kinetic of pure PP and flame-retarded (FR) PP by using Kissinger method, Flynn-Wall-Ozawa and Coats-Redfern (Coats and Redfern, 1964) methods. The results confirmed that the activation energy of PP and FR PP obtained by Kissinger method agrees well with that obtained by Coats-Redfern method. Paik and Kar (2009) studied polyethylene particles of nanometer and micrometer size. It was observed that E_α and lifetime of nano sized polyethylene particles was higher than micro polyethylene particles. Several methods for the calculation of kinetic parameters of thermal degradation by TGA have been developed. They can be classified into three categories: differential, integral and direct methods on the basis of Arrhenius equation. Another way of classification of methods for calculating the kinetic parameters is: single heating rate methods and multiple heating rate methods. Friedman, Freeman-Carroll and Coats-Redfern (Coats and Redfern, 1964) are single heating rate methods, whereas Flynn-Wall, Ozawa (Ozawa, 1965), Kim-Park and Kissinger are multiple heating rate methods. The third classification of methods for the analysis of kinetic parameters is either model fitting or model free methods. Freeman-Carroll and Coats-Redfern are model fitting methods and Flynn-Wall, Kim-Park and Kissinger are model free methods. On the bases of thermal condition, thermal degradation kinetic methods can be classified into isothermal.

and non-isothermal methods. The conventional and standard method is isothermal method whereas Friedman, Freeman-Carroll, Kissinger and Flynn-Wall are non-isothermal methods. The model-fitting methods were widely used for solid-state reaction because of their ability to directly determine the kinetic parameters from a single TGA thermogram, but in recent years, the use of model-free methods have been reported (Premkumar et al., 2005; Vyazovkin and Wight, 1999; Yu et al., 2004). Model-fitting methods produce unreliable, and sometimes nonsensical results. For more accurate measurement, model-free methods may be applied to assess the dependence of activation energy on the degree of conversion, which can be correlated with the investigated process mechanism. The advantage of the model-