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Impact of modified graphene and microwave irradiation on thermal stability and degradation mechanism of poly (styrene-*co*-methyl meth acrylate)

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ABSTRACT

Poly (styrene-*co*-methyl methacrylate) [P(st-mma)] composite containing 0.1 wt% modified graphene (MG) was prepared via melt blending. MG was prepared by oxidation method using nitric acid. The P(st-mma) and P(st-mma)MG composite were irradiated using microwave radiation. The degradation mechanism and thermal stability of the irradiated and un-irradiated samples was analyzed by TGA. P(st-mma)MG showed high thermal stability. The average activation energy of thermal degradation was found to be 200 kJ/mol for P(st-mma), 214 kJ/mol for P(st-mma)MG. The activation energy was highest for 10 min irradiated nanocomposites indicating an improvement in stability. The degradation mechanism was investigated by comparing the master plots constructed using the experimental data with theoretical master plots of various kinetic models. The thermal degradation of P(st-mma) and P(st-mma)MG composite before and after irradiation governs the random scission mechanism. SEM and TEM micrographs showed improved interactions and degradation of composites after 10 min and 20 min irradiation respectively.

1. Introduction

Ever since its discovery, graphene has attracted increasing interest in the development and investigation of various properties of its reinforced polymer composites [1–4]. A Graphene, sp^2-hybridized carbon atom, arranged in two dimensional densely packed honey comb crystal lattice, possesses superior thermal, mechanical and electrical properties [5–7]. These extra ordinary properties motivated attention to incorporate graphene in polymer matrix and thus tailor the final properties of the composite [8–12]. Consequently, a polymer-graphene composite can be utilized in various potential applications such as super capacitors [13], bio materials [14], batteries [15], and microelectronics [16].

The most challenging objective in the development of polymer composite is to achieve complete dispersion and efficient interaction of nanomaterials with the polymer chains which result in full enhancement of final properties of polymer composites. Different studies have been performed such as functionalization of nanomaterials [17,18], implication of small polymer chains [19] and addition of peroxide during melt mixing [20], but the researchers are still investigating the more cost effective and green technique to attain better interaction between nano fillers and a polymer matrix.

The irradiation technique is widely used and accepted for pyrolysis of polymers [21]. Nowadays microwave radiation has proved to be a fast, economical and green technique for the synthesis of various polymer composites. However, very few studies [4,22,23] have been performed to investigate the behavior of microwave irradiation on the enhancement of the polymer matrix and graphene interaction.

The thermal stability of the polymer composites is a key factor for their applications in high temperature environments. Therefore it is highly important to assess the thermal stability of the composites. Investigation of the thermal stability of the materials under different conditions can be predicted by studying the kinetics of thermal degradation. [24–26] An accurate kinetic analysis requires the determination of kinetic of triplet (i) activation energy E_A, (ii) pre exponential factor A, and (iii) the kinetic model $f(\alpha)$. This latter parameter, also known as conversion function, is an algebraic form associated with the physical model that demonstrates the kinetics of solid state reaction [27,28].

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Despite numerous studies, the phenomenon of degradation of polymer and its composite is still under investigation. Most of the studies have considered model free methods [29,30] and 1st or *n*-order model [31,32] to study the kinetics of thermal degradation of polymers. However recent studies have found that the thermal degradation of polymer is not only associated to a 1st or *n*-order model but polymer degradation can mostly be controlled by diffusion or a random scission mechanism [33,34].

In this study the thermal stability and degradation kinetics mechanism of poly (styrene-*co*-methyl methacrylate) was investigated in the presence of modified graphene and microwave irradiation. The copolymer was blended with modified graphene via a melt blending technique and irradiated using microwave radiation for different periods. The effect of modified/functionalized graphene and microwave irradiation on the thermal stability and evaluation of kinetic degradation model was studied.

1.1. Theory

Solid state reaction can be generalized as [35]

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α, k *and* $f(\alpha)$ represents the extent of conversion, the rate constant and the reaction model in differential form respectively. For non-isothermal case, the temperature variation can be included in form of heating rate β as shown below;

$$\frac{d\alpha}{dT} = \frac{k}{\beta} f(\alpha) \tag{2}$$

$f(\alpha)$ and k depends on the extent of conversion and temperature respectively. The temperature dependent function follows the Arrhenius relationship

$$k = k_0 Exp\left[-\frac{E}{RT}\right] \tag{3}$$

Hence, the determination of $f(a)$, k_o and E is required to describe the progress of a reaction either with time or temperature dependence. Standard functions, representing particular and physically meaningful ideal reactions have been developed and are listed in Table 1 [34].

1.2. Determination of activation energy

The activation energy can be determined either by model-fitting or model free methods. The model-fitting methods are criticized, especially in case of solid state kinetics. The reason for such criticism is based on the fact that the physical state of system is changing with the time or temperature. Hence, assuming constant activation energy might lead to erroneous and uncertain results [36–38]. The use of model-free or the *iso*-conversional methods is encouraged in case of solid state kinetics. Although these methods required multiple heating rates data, the assumption of a kinetic model is not required [39–42]. The model-free methods can also provide detailed insights of the reaction progress from the conversion and temperature dependence. The differential Friedman method [43] given by the Eq. (4) is utilized in this case. For more details of the methods, or for calculation of activation energy and their accuracy, readers can refer to [35].

$$\ln\left(\beta_i\left(\frac{d\alpha}{dT}\right)\right)_\alpha = -\left[lnf(\alpha) + \frac{E_A}{RT_i}\right] \tag{4}$$

Thus for experiments performed at variant linear heating rates β, $f(a)$ will be a constant at a fixed value of (α). Therefore by measuring the temperature (T_i) and the rate of transformation at a fixed

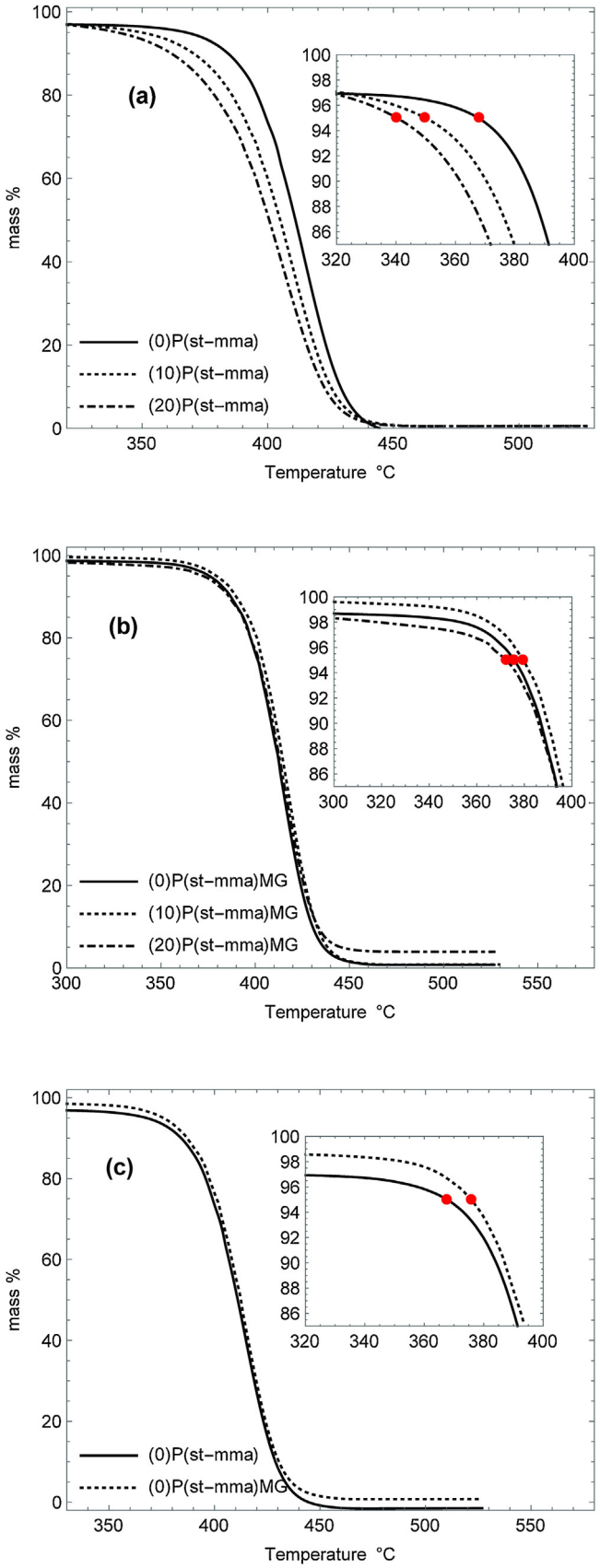

Fig. 1. Weight loss as function of temperature obtained from TGA: (a) P(st-mma) irradiated for different time periods, (b) P(st-mma)MG irradiated for different time periods, (c) comparison of P(st-mma) and P(st-mma)MG composites, Red circles indicates the temperature at 5 wt .% loss. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)