

Thermal properties of ethyl vinyl acetate (EVA)/ montmorillonite (MMT) nanocomposites for biomedical applications

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Abstract. The viability of nanocomposites comprising Ethyl Vinyl Acetate (EVA) filled montmorillonite (MMT) nanoclay as candidate materials of biomedical devices was investigated. EVA/MMT nanocomposites were prepared by incorporating the ratios 0, 1, 3 and 5% of organoclay MMT to EVA copolymer. In vitro biostability of the neat EVA and EVA nanocomposites was compared and assessed by exposing the materials to oxidizing and hydrolytic agents for 4 weeks at 37°C. The thermal properties of the neat EVA and EVA nanocomposites nanoclay filled were studied by using thermogravimetric analysis (TGA). TGA results indicate that the EVA nanocomposite sample containing 1 wt% MMT exhibits higher T_{onset} and significant reduction in the rate of mass loss as compared to the neat EVA and other nanocomposites.

1 Introduction

In today's world, medical devices contribute significant role in enhancing the quality and efficacy of healthcare. While several strategies are being sought for upgrading the quality of health care, however, medical device designers are facing an issue with a limited number of off-the-shelf materials that can be designed for biomedical devices, especially those implantable materials for long term application [1].

EVA is a synthetic random copolymer of hydrophobic ethylene and hydrophobic vinyl acetate monomers. It is one of the most used polymers for a wide area of applications. Due to its unique and wide range properties, researchers have discovered the promised prospects of this polymer as well as its composites in healthcare and medical applications [1]. Generally, EVA has been accepted for biomedical applications due to its random structures, which offer high ozone resistance, weather resistance, and exceptional mechanical

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properties [2]. Nowadays, EVA comes into its emerging role as a controlled release excipient for biological systems [1].

The incorporation of nanoclay or layered silicate into polymers to obtain nanocomposites were one of the important studies since 1950. However, wide interest in the nanocomposite research area has started over forty years later. That was when the research team at Toyota Central Research & Development Co., added MMT (5%) as nanofiller into the Nylon-6 matrix, which caused an increase in the strength of the material [3]. Depending on nanoclays type, the low aspect ratio type ones such as hectorite may have an average platelet length that is approximately 30 nm. However, the larger type such as fluoromica may have an average platelet length up to 2000 nm.

Nanocomposites incorporating nanoclays as filler have been produced mostly for industrial, automotive and packaging purposes [4]. However, less attention has been paid for biomedical applications. Styan (2006) demonstrated the permeability of the thermoplastic polyurethane matrix to water and oxygen molecules was successfully reduced by the addition of the organically modified clay [5]. In a more recent publication, Styan et.al (2012) highlighted that the addition of MMT modified with amino undecanoic acid resulted in enhanced biostability of this particular matrix. They hypothesized that the presence of the impermeable organoclay layers led to a 'barrier effect', which can restrict the access of degradable species to the polymer structure, thus reducing the nanocomposite's oxidative degradation rate [6]. Andriani et.al studied the in vitro biostability of polyurethane containing organically modified clay (organoclay) with different types of surface modification. They found that the nanocomposite incorporating the most hydrophobic organoclay resulted in greater biostability by hindering greater extent of matrix surface re-structuring upon oxidative exposure [7]. These findings show that the barrier properties of the polymers may be impacted by the organoclay, thus can be controlled to enhance the biostability. These properties are highly needed for materials insisted for use in biomedical applications.

An investigation on in vitro biostability and biocompatibility of ethyl vinyl acetate (EVA) nanocomposites incorporating organically modified montmorillonite (organo-MMT) as a new material for biomedical applications [8]. They studied the effect of oxidizing and hydrolytic agents on the morphology and mechanical properties of EVA/MMT nanocomposites. In this study, the thermal behaviour of EVA/ MMT nanocomposites prepared by melt compounding process and exposed to H₂O₂ as an oxidizing agent was investigated as a new candidate of biomedical applications.

2 Experimental

2.1 Materials

EVA was supplied by UBE-Maruzen Polyethylene Co. Ltd., Tokyo, Japan and commercially known as UBE EVA V215. The weight percentage of vinyl acetate is 15%, with the rest is ethylene. Organically modified montmorillonite (organo-MMT), which contains 35–45 wt% dimethyl dialkyl (C14–C18) amine as an organic surfactant, was manufactured by Sigma-Aldrich (USA) and supplied by Zarm Scientific and Supplies Sdn. Bhd. Hydrogen peroxide H₂O₂, 30–32 % solution (Qrec®), was supplied by Qrec (Asia) Sdn. Bhd. Phosphate-buffered saline (PBS) tablets were manufactured by Sigma-Aldrich and used as the hydrolytic agent after being dissolved in distilled water.

2.2 Preparation of the samples.

The samples were prepared by using a Brabender Plasticorder machine manufactured by Lab Tech Co. (LZ80). EVA was mixed with different ratios of organo-MMT nanofiller (0, 1, 3, and 5%) at 160 °C prior to drying the starting materials for 24 hours at 50 °C. The resulting nanocomposite samples were then compressed into 1 mm thick sheets using compression moulding machine model GT-7014-H30C from GOTECH Co. The samples after that were cut accordingly for testing and analysis.

2.3 Thermal Gravimetric Analysis (TGA).

TGA analysis was carried out by Perkin Elmer Pyris Diamond TG/DTA Thermogravimetric Differential Thermal Analyzer. 10 ± 1 mg of each sample was subjected to analysis of temperature ranging from 30 - 650 °C, heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere which was pumped into the system at a flow rate of 30 ml min^{-1} .

3 Results and discussions

TGA was employed to study and compared the thermal stability of neat EVA and EVA nanocomposites. The thermal stability in this study is based on the temperature when the neat EVA and EVA nanocomposites start to degrade (T_{onset}) and the rate of mass loss. Figure 1 and Figure 2 display the TGA and DTG curves of the neat EVA and EVA nanocomposites, before and after H_2O_2 treatment, while Table 1 summarizes the thermal degradation onset temperature (T_{onset}) of all the materials.

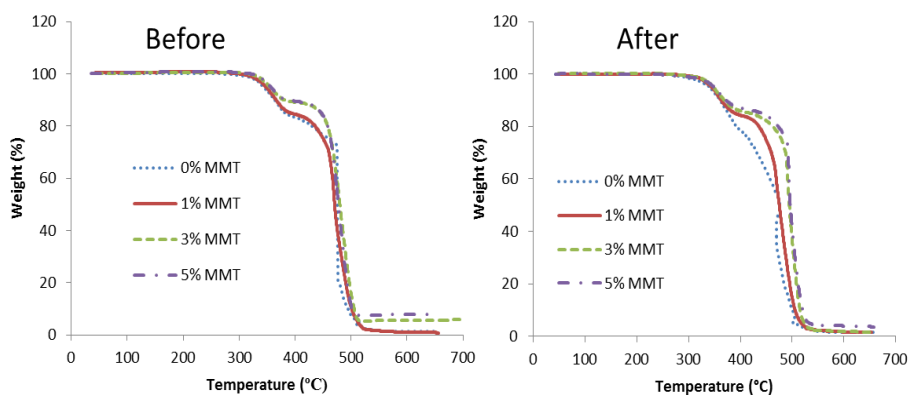


Fig. 1. TGA curves of EVA and EVA nanocomposites before and after H_2O_2 exposure at 37°C.

The intensity of the derivative thermogravimetric (DTG) peaks depends on the amount of degradation product released, which is attributed to the degree of interaction between the EVA polar and nonpolar segments, and also the EVA-nanoclay interactions. Based on Figure 1, the decomposition of neat EVA copolymer and EVA nanocomposites took place in two steps. The first mass loss step between 200 and 300°C was due to deacetylation process, where the release of gaseous acetic acid and formation of carbon-carbon double bonds along the polymer backbone occurred. The second mass loss step (between 400 and 500°C), was due to the oxidation and volatilization of hydrocarbons resulting from the decomposition of the EVA copolymer backbone [9].

For TGA of neat EVA and EVA nanocomposites before the exposure, T_{onset} of a first degradation step of EVA nanocomposites occurred at lower temperatures as compared to neat EVA, and this was due to the degradation of the organic surfactant [9]. The degradation of dimethyl dialkyl (C14-C18) amine, that used to surface modified the MMT accelerated the degradation of acetic acid. The T_{onset} of second degradation step of EVA nanocomposites incorporating 3 and 5 wt% MMT occurred at a higher temperature than that of the neat EVA and EVA containing 1 wt% MMT.

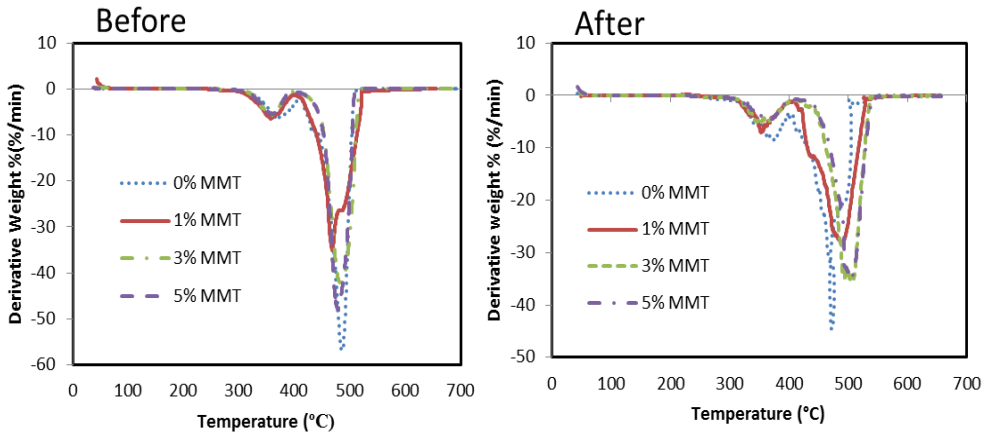


Fig. 2. DTG curves of neat EVA and EVA nanocomposites before and after H_2O_2 exposure.

Table 1. Thermal degradation onset temperature of EVA and EVA nanocomposites before and after the in vitro treatment in oxidative agent (H_2O_2) at 37°C .

Material	T_{onset} ($^\circ\text{C}$)			
	First step mass loss		Second step mass loss	
	Before	After	Before	After
0%	265	240	420	405
1%	240	235	415	410
3%	255	235	425	425
5%	264	230	430	445

TGA of neat EVA and EVA nanocomposites after in vitro exposure to H_2O_2 at 37°C show that T_{onset} of first degradation step for the neat EVA and EVA nanocomposites was seen to occur at lower temperature after the in vitro exposure due to degradation process. The in vitro exposed nanocomposites exhibit the same thermal behaviour as the non-exposed nanocomposites, as they show lower T_{onset} than the neat EVA. The T_{onset} of second degradation step for the neat EVA and EVA containing 1 wt% MMT was seen to occur at lower temperature after the in vitro exposure. This is expected to happen as a result of polymer degradation upon oxidative exposure. However, the incorporation of 1 wt% MMT into the EVA matrix resulted in an enhanced thermal stability, as the nanocomposite exhibits higher T_{onset} and significant reduction in the rate of mass loss. This suggests that the incorporation of 1 wt% MMT contributes to biostability enhancement of the EVA matrix, which is in good agreement with SEM analysis and tensile test results. The well dispersed and exfoliated organo-MMT may restrict the entrance of the oxidant molecules into the polymer chains and prevent them from undergo a more severe degradation process. It is interesting to note that the nanocomposites with 3 and 5 wt% MMT show an

anomalous thermal behaviour. No reduction in thermal stability upon the in vitro exposure occurred, and in the case of nanocomposite with 5 wt% MMT, the increase in Tonset was observable. As opposed to the previous XRD, TEM, SEM and mechanical performance data, these TGA results suggest that improved thermal stability was obtained with the incorporation of 5 wt% MMT. Thus, further studies are needed to elucidate this phenomenon.

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