International Journal of Current Science, Engineering & Technology ISSN : 2581-4311
Original Research Article | Open Access | AMCT 2017 Malaysia | *Special Issue*

Tensile Properties of γ Irradiated And Non-Irradiated Poly (L-Lactide) Carboxymethyl Starch And Nano-Hydroxyapatite Composite Film

Mohd Reusmaazran bin YUSOF[1,a*], Roslinda SHAMSUDIN[1,b], Yusof ABDULLAH[2,c] and Norzita YAACOB[1,d]

[1]Department of Applied Physics, Faculty Science and Technology, Universiti Kebangsaan Malaysia, 43600, UKM Bangi, Selangor, Malaysia

[2]Materials Technology Group, Industrial Technology Division, Malaysian Nuclear Agency, 43000, Kajang, Selangor, Malaysia

[a*]reusmaazran@nm.gov.my, [b]linda@ukm.my, [c]yusofabd@nm.gov.my, [d]norzita@nm.gov.my

Abstract. A film of poly (L-lactide) (PLLA), carboxymethyl starch (CMS) and nano-hydroxyapatite (nHA) was prepared by casting evaporation method. The use of natural resources of CMS blending with PLLA induced the pore in the potentially used in tissue engineering applications. PLLA were blend with CMS in a solution form and added with nHA particles. The film was irradiated with gamma (γ) at 10, 30, 50 and 80 kGy doses. Pores with diameter in the range of approximately 20-50 μm was observed. Low tensile strength was obtained CMS was introduce into PLLA matrix, however improves by addition of nHA. Increasing of γ irradiation exceeded 10 kGy leads to decreasing in tensile strength. Glass transition temperature, T_g, crystallization temperature, T_c and enthalpy of crystallization indicating the changes in degree of crystallinity due to the degradation occur in when the samples were undergo irradiation.

Keywords: *PLLA, PLLA/CMS, PLLA/CMS/HA, Gamma irradiation, Tensile strength;*

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

DOI: ***10.30967/ijcrset.1.S1.2018.209-214***

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia;

1. INTRODUCTION

PLLA is linear aliphatic polyester with a large number of applications ranging from medical implant material, drug delivery system and tissue engineering scaffold. PLLA as much great interest due to its biocompatibility, biodegradability and proven to be safe use in human body. Successful application as medical implant makes this material more attractive and also to be modified with other material to improve their applications in the medical field [1]. The blending PLLA either with other polymeric material or composited with other material has been main subject to many researcher recently. PLLA blending with PDLA [2], PLLA and PLCL as a scaffold materials[3], DLLA-PEG-PDLLA-b-PLLA used as a drug delivery system [4], PLLA and HA/TCP [5-8] and PLLA/MgO composite [9]. The used of ionizing radiation were also been implemented either to induce the cross linking or to tailor the degradation profile of implant material [10-12].

The properties of the PLLA and many polymeric material including mechanical behaviours, thermal and degradation properties are strongly depend to the crystalline and morphology. The crystallization rate of PLLA is very slow; meaning that it is very hard to achieve high crystallinity in PLLA[13]. Blending with other polymer, composited with other material and the application of ionizing radiation such electron beam [14,15], and gamma radiation [16-18] be able to modify its crystallization. It is well known that the biodegradability of PLLA is strongly related to its crystallinity, high order structure, blending ratio and morphology. Inside the body, PLLA degrade to lactic acid through chain scission due to hydrolytic attack on their ester bond and enter tri-carboxylic acid cycle follow by metabolism process and subsequently eliminated from the body as carbon dioxide and water.

The aim of this works is to study the blending between the PLLA, CMS and nHA in the form of porous film. Recently the blend of natural polymer and synthetic for both organic and in-organic resources were synthesized from sago starch widely used in pharmaceutical product and wound healing materials and food technology. CMS remain as alternative to synthetic polymer due to its biocompatibility, degradable, non-toxic and inexpensive as well. CMS commonly produce via synthesis by chemical modification reaction. Carboxymethylation process of starch is one of the procedures to functionalize this material to provide valuable properties as biomaterial. During carboxymethylization the hydroxyl group(O-H) in starch molecule was substituted with carboxymethyl group (CH_2COOH) to produce CMS[19]. In this study the PLLA, PLLA/CMS and PLLA/CMS/HA film were prepared by solvent casting evaporation techniques. The tensile properties of PLLA with addition with CMS and nHA at various irradiation doses were investigate.

2. MATERIALS AND METHODS

PLLA with inherent viscosity 2.32 dl/g were obtained from BioInvigor (Taipe, Taiwan). Nano-Hydroxyapatite with particle size less than 200 nm was purchased from Sigma Aldrich (USA). CMS was prepared from local sago starch. Sago starch was slurred in 300 ml of isopropanol added with NaOH about 30% in reactor flask equipped with reflux condenser and burette. In this work, the detail carboxymethlyzation process of sago starch was done as described by Yaacob et al. [19]. 7% concentration PLLA were prepared by dissolving the granule PLLA in dichloromethane. Films were prepared by casting evaporation method by mixing 20% of CMS v/v in with present of 0.1% of nHA. They were mixed and then stirred for 24 hours later rolled to form a film of 200 µm thickness and dried for 24 hours. The thickness of the film reduces in the range of 50 - 70 µm after the drying process.

Samples were irradiated at different doses of 10, 30 50 and 80 kGy. Irradiations were carried out in research loop facility at Malaysian Nuclear Agency Gamma Sterilization Plant with ^{60}Co sources. The irradiation was carried out at dose rate 1.67 $kGyh^{-1}$, the measurement of dose rate by using cerric cerous dosimeter in order to measure the effectiveness of doses absorbed by samples.

Changes in thermal properties, glass transition temperature (T_g), cold crystallization temperature (T_c), melting temperature (T_m), enthalpy of crystallization (H_c) and enthalpy of melting (H_c) were investigated using TA Instrument (Q20, USA). Samples were purged with nitrogen gas approximately 35 ml min^{-1} to avoid any oxidation during the heating. About 2.35 mg samples were heated from 20 to 300 ^0C at the heating rate of 10 $ºC\ min^{-1}$.

The SEM (Quanta 400, FEI, USA Germany) was used to evaluate the morphology of film porosity. The images were collected at 2000x, magnification at 10 kV. Tensile testing was conducted using 50 N load cell (Model UUK 5, Korea) equipped with Ezi Step micro stepper motor system (Fastec, Korea). A screw type crosshead and attached with data logger OMRON RX-RX25. The elongation was determined by 1.0 mW Omron laser detector with detection limit 2.5 ms $600nm^{-1}$. The tensile test conducted at 0.5 mm min^{-1} of crosshead velocity. Samples were punch into rectangular shape with dimension of 5 x 40 mm. Stress and strain curve were then calculated based on the thickness of the film.

3. RESULTS AND DISCUSSION

The films that produce by cast evaporation technique segregate into two layer; polymer rich phase and polymer leans phase due to the 3 phase system which are PLLA, CMS and nHA particles. CMS is not dissolve in PLLA solution because of the different solvent. PLLA is hydrophobic whereas nHA and CMS have a hydrophilic structure. During evaporation polymer rich phase is transform into matrix and polymer lean phase will produce the porous structure [20]. Fig. 1 shows the pore induced in PLLA/CMS and PLLA/CMS/nHA compared to dense film of PLLA of none irradiated samples. Generally, introducing the CMS into PLLA reduced the tensile strength due to the generating of porous structure within the sample. Tensile properties can be improved by addition of HA nano particle (nHA). From our observation, PLLA matrix contributes most to of the properties to bulk composite sample. Fig. 2(a) exhibits tensile strength of the PLLA/CMS/nHA, PLLA/CMS and PLLA samples for non-irradiated and irradiated samples at various irradiation doses.

Porosity affected the tensile property by reducing the strength by 55% from 34.4 to 15.2 MPa for non-irradiated PLLA and PLLA/CMS respectively. Addition of nHA in PLLA/CMS sample reducing the porosity therefore increase the tensile strength up to 28.4 MPa. The morphology of the PLLA/CMS/nHA samples as shown in Fig. 1(c). Another possible reason to the increasing of tensile strength is the ability of nHA penetrating the amorphous region thus prevent mobility of the polymer chain during tensile test [21,22].

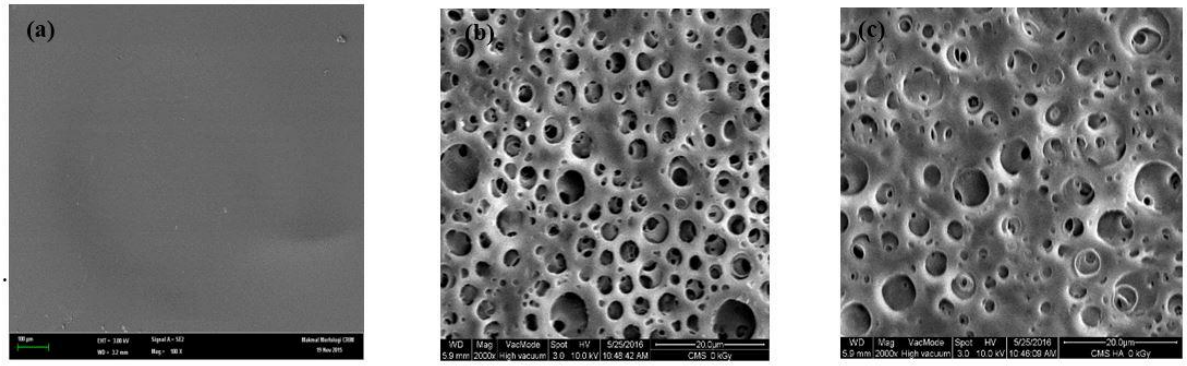

Fig 1 The SEM micrograph of (a) PLLA, (b) PLLA/CMS and (c) PLLA/CMS/HA of non-Irradiated sample produced by casting evaporation method.

Tensile strength was observed reducing in all irradiated samples except for sample irradiated at 10 kGy (Fig.2). The tensile strength increase about 23%, 44% and 6.5% at lower doses (10 kGy) and reduce down about 27%, 15% and 28.7% at higher doses (80 kGy) for PLLA, PLLA/CMS, and PLLA/CMS/HA, respectively. The effect of ionizing radiation to polymer either can be degradation or crosslinking, in fact this mechanism can occur simultaneously [12,16,23]. If the chain scission is pre dominant than the crosslinking, the degradation will be take places. Massive degradation will lower the mechanical strength in contra to the crosslinking [23,24].

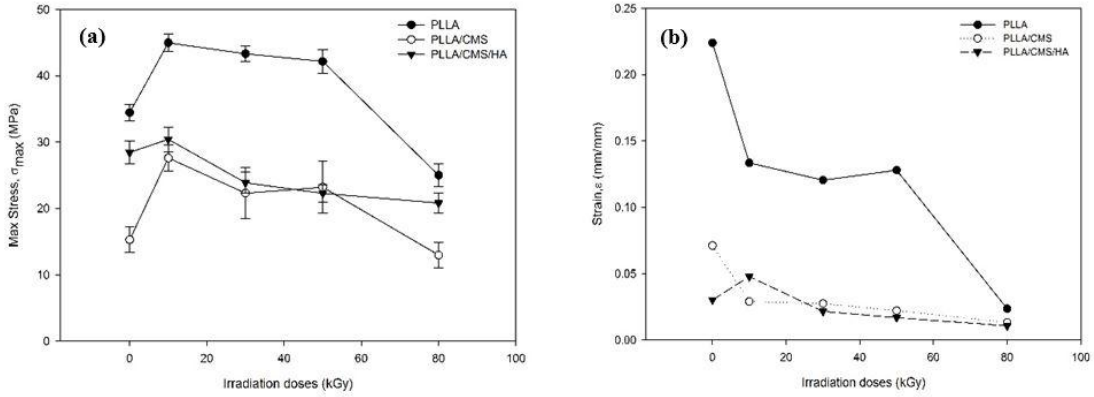

Fig. 2 (a) The ultimate strength and (b) Strain of PLLA, PLLA/CMS and PLLA/CMS/HA of both non-irradiated and irradiated at 10 and 80kGy

The possible reason of increasing in tensile strength at 10 kGy is suggested due to some part of the polymer chain occure a crosslinking as in the increasing of T_m as indicate in DSC thermogram (Fig 2b) [11].

The present of nHA particle in the sample promoting the stiffness and reduce the plasticity thus reduce in strain. Fig 2b exhibits the decreasing in strain when nHA was introduce in PLLA/CMS. nHA penetrated into amorphous region thus retarded the movement of the molecular chain with the sample and increased the stiffness which lead to the brittle failure of PLLA/CMS/nHA sample [22]. Nano HA particles together with irradiation would destroy the molecular to shorter chain with open structure that lead to rapid failure.

The thermal stability of PLLA and PLLA/CMS/nHA were investigated via DSC thermogram for both irradiated and non-irradiated samples as shown in Fig. 3. PLLA is a semi crystalline polymer, exhibits both endothermic and exothermic peaks which attribute to amorphous and crystalline region. The crystalline region consists of more oriented chains and closely pack compared to amorphous regions [25,26]. Peaks appeared at 63.6, 104.2 and 157.5 ºC for the PLLA samples corresponding to temperature of glass transition, T_g, cold crystallization, T_c and melting, T_m. The T_g values was slightly lower when PLLA was blended with CMS and also in addition of nHA. By irradiating the samples the T_g were significantly decrease and even more by decreasing the doses to the increasing of irradiation doses. The decreasing of T_g values can be explained by degradation that occurred in the amorphous region from fragmentation of polymer chain [13,24].

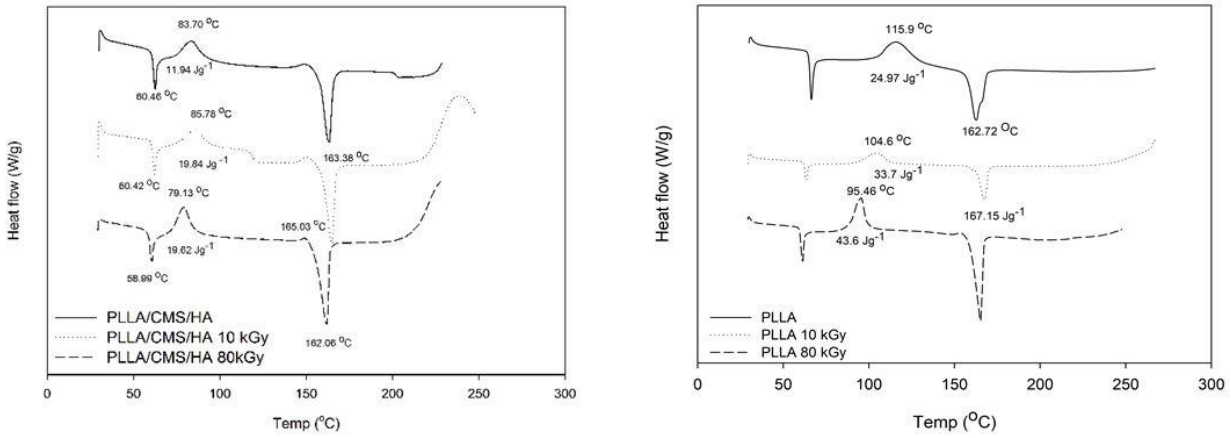

Fig. 3 DSC thermogram of irradiated and non-irradiated samples, (a) PLLA and (b) PLLA/CMS/nHA at 10 and 80kGy

The increasing of crystallization peak after irradiation process can be explained by the increasing of the crystallization enthalpy. The sharp peak indicated that higher rate of crystallization upon heating. The energy from the ionizing radiation resulted in chaining scission due to energy exceed the electron binding energy [27]. The polymer chain is fragmented into shorter chain, the higher the energy received the shortest the chain, this is known as degradation mechanism [24]. During heating, the fragmented chain re-oriented into a crystallization phase. Shorter chain would increase the crystallization rate thus produced the sharp peak in DSC thermogram. The more fragmentation occurs the higher enthalpy produce during heating in DSC analysis as exhibited in Fig 3a. Higher doses (80 kGy) produce sharp crystallization peak indicated the occuring of a massive degradation. The crystallization enthalpy of PLLA increased from 24.9 to 43.7 Jg^{-1} for non-irradiated and irradiated samples at higher doses respectively, and 11.9 to 19.2 Jg^{-1} for PLLA/CMS/nHA. The fragmentation of the of the chain would ease the mobility of the molecule prior to heat and lower the T_g (Fig. 3). The T_g value decreased from 63.6 to 59.8 ºC for PLLA and 60.9 to 58.1 ºC for PLLA/CMS/nHA for pre and post irradiation at 80 kGy.

Partially chain scission occurred at lower doses because of low energy received by the polymer chain: If took place only in amorphous region, retarded the mobility of the polymer chain upon heating and increased in tensile strength at lower doses [25]. Loo et. al. [25] suggested that, the polymer chain in the crystalline region were close one another, the free radical either hydroxyl group or alkyl will trap in crystalline region

promote recombination. The recombination within the free radical would prevent the degradation thus contributed to the increasing of tensile strength.

4. SUMMARY

The PLLA/CMS/nHA porous film were produced by casting evaporation method subsequently irradiated by γ at various irradiation doses. Introducing CMS into PLLA matrix reduce the tensile strength due the present of porosity and can be improved by addition of nHA. Lower irradiation doses may increase the tensile strength whereas higher irradiation doses reduce the strength of samples due to massive destruction in polymer chain. DSC thermogram indicated the degradation occurs at higher doses.

ACKNOWLEDGEMENT

Financial supports from Dana Impak Perdana (DIP 2015-017) of Universiti Kebangsaan Malaysia, Ministry of Higher Education are gratefully acknowledged.

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