Modification of Tensile and Impact Properties of Crosslinked Rubber Toughened Nanocomposites via Electron Beam Irradiation

N.A. Jamal, H. Anuar and S.B.A. Razak

Abstract - *Enhancing the tensile and impact properties of high density polyethylene (HDPE)/ethylene propylene diene monomer (EPDM) matrix is the main target of developing nanocomposite. The nanocomposite system was first prepared via melt intercalation method with different organophilic montmorillonite (OMMT) loadings. Electron beam (EB) irradiation was applied as a crosslinking agent for modification of tensile and impact properties of HDPE/EPDM matrix and HDPE/EPDM filled OMMT systems. The effectiveness of EB irradiation technique were then compared with control one (uncrosslinked system) and analyzed based on the tensile and impact tests as well as morphological examination. The tensile and impact tests revealed that control and EB irradiated systems had attained the optimum tensile and impact properties at 4 vol% OMMT content. EB irradiated system at dose rate of 100 kGy showed excellent in tensile and impact properties with the highest crosslinking degree which were proved by gel content analysis. X-ray diffraction (XRD) analysis confirmed the existence of delamination structure with EB irradiation technique based on the disappearance of characteristic peak. The degree of delamination was further investigated by transmission electron microscope (TEM).*

Key Words - Tensile properties; Impact property; Organophilic montmorillonite; Electron beam irradiation; Gel content

I. INTRODUCTION

Studies on polymer matrix filled nano filler have been widely investigated due to its outstanding properties. These polymer layered silicate (PLS) nanocomposites can attain a certain degree of stiffness, strength and barrier properties with far less ceramic content than comparable glass or common inorganic reinforced polymers [1-4]. Although other solids can be used, the most common reinforcements currently used to make nanocomposites are natural silicates, such as mica, montmorillonite, kaolinite, saponite and hectorite [4]. As most nano filler is hydrophilic in nature, they are known to be incompatible with hydrophobic polymer matrix. A general approach to alleviate such phenomenon is by the introduction of crosslinking agent or so called compatibilizer agent. Most researchers introduced compatibilizer agent by means the use of chemical agents such as maleic anhydride grafted polymer (MA-g) plastic resin, silane agent and so on [2-6].

In the current study, instead of using chemical agent, physical crosslinking agent by means of electron beam irradiation (EB) has been introduced to enhance the compatibility between the polymer matrix and nano filler. EB irradiation offers similar or even better advantages as compared to crosslinking agent by means of chemical agent. The property enhancements achieved include improved mechanical and properties, increased chemical and solvent resistance. Chain crosslinking and scission are the two reactions that occur during EB processing of polymers. Polymers typically undergo simultaneous scission and crosslinking, but in most cases with one or the other clearly predominating [7-10].

Crosslinking is the intermolecular bond formation of polymer chain. The degree of crosslinking is proportional to the radiation dose [8, 9]. On other word, polymer chains of different component are connected to one another by the crosslinking bonds to form a rigid three dimensional network. Much works have been done on radiation crosslinking of uncrosslinked polymers and crosslinking of various rubbers and plastics by electron beam irradiation [7-10]. In contrast, scission is the opposite process of crosslinking in which the rupturing of carbon-carbon bond occurs. Scission reduces crosslinking efficiency and degrades the properties of polymers (chemical resistance, mechanical and thermal properties).

Polymer matix for the current system consists of blending high density polyethylene (HDPE) and ethylene propylene diene monomer (EPDM) at the ratio of 70% of HDPE to 30% of EPDM. Different clay loadings are varied between 2, 4, 6 and 8 vol% for the development of nanocomposite system. Therefore, the current study aims to vary and highlight the interest of EB irradiation technique for HDPE/EPDM, where unfilled composites and nanocomposites were prepared with different irradiation doses rate between 50, 100, 150 and 200 kGy. The results obtained for the EB irradiated system were then compared with control system in order to determine the optimum system.

II. EXPERIMENTAL DESIGN

A. *Materials Selection*

Homopolymer high density polyethylene (HDPE) (Melt index 3-6 g/10min, density 900 kg/cm^3) supplied by Cementhai Chemicals Group, Thailand and Ethylene

Propylene Diene Monomer (EPDM) supplied by Centre West Sdn Bhd, Malaysia were used as the base polymer matrix. Commercially available organophilic montmorillonite (OMMT) surface modified with 15-35 wt% octadecylamine and 0.5 wt% aminopropyltriethoxysilane obtained from Sigma-Aldrich Group, Malaysia was used as reinforcing agent to prepare nanocomposites.

B. *Compounding*

Melt blending of HDPE (70 vol%), EPDM rubber (30 vol%) and OMMT content at different loadings between 2, 4, 6 and 8 vol% was carried out in an internal mixer (Thermo Haake Rheomix 600P). Prior to mixing, the matrix polymer and the nanoclays were dehumidified in a dry oven at 110 ^{0}C for a period of 1 hr.

C. *Specimen Preparation*

Subsequently, the blended samples were compression molded as per ASTM-F-412 using a compression molding machine at a temperature range of 135–155 ^{0}C with 8 tone metric pressures for 14 min.

D. *High Energy EB Irradiation*

The melt compounding samples were exposed under high energy EB irradiation at different doses rate of 50, 100, 150 and 200 kGy at room temperature by using 3 MeV electron beam accelerator. The acceleration energy, beam current and dose rate were set to 2 MeV, 2 mA and 50 kGy/pass respectively. Details on the composition, parameters and modification of HDPE/EPDM and HDPE/EPDM filled OMMT are summarized in Table I.

III. CHARACTERIZATION TECHNIQUES

E. *Mechanical Tests*

Test specimens for analyzing mechanical properties were initially conditioned at 23 ± 1 ^{0}C and 55 ± 2 % relative humadity (RH) for 24 hr prior to testing. These conditioned specimens were subjected to mechanical testing was performed on 10 samples and an average readings of 5 samples reading were recorded. The corresponding standard deviation along with the measurement uncertainty value for the experimental data showing maximum deviation was also included.

F. *Tensile Test*

Specimens with dimensions of 125 × 1 × 1 mm^3 were subjected to a tensile test as per ASTM F412, using Instron 5567 machine with 5 kN load. Crosshead speed and gauge lengths were set to 50 mm/min and 60 mm.

G. *Impact Test*

Notched Izod impact test as specified by ASTM D256 standard test method was applied by using Ceast 6545/000 model. Specimens with 62 x 15 x 3 mm^3 dimension were subjected to an impact test with 2.54 mm depth of notch. Before the testing takes place, each sample is immersed into liquid nitrogen for about 30 seconds. The energy absorbed by the specimen in the breaking process is known as the breaking energy (J/m).

H. *Gel Content Analysis*

The gel content of the samples was determined by boiling the samples with xylene for 24 hours in accordance to ASTM D2765 procedure. The extracted samples were vacuum dried to constant weight for 16 hours at 75°C. The gel content was calculated as the ratio of weight of dried sample after extraction to the initial weight of the sample before extraction. The results reported were the average of three specimens. The gel content percentage of crosslinked samples was calculated using the formula below:

$$(\%)\ \text{Gel content} = \frac{\text{weight after extraction}}{\text{weight before extraction}} \times 100$$

I. *X-Ray Diffraction Analysis (XRD)*

X-ray diffractograms of OMMT and the nanocomposites were recorded using Shimadzu 6000 (Japan), X-ray crystallographic unit equipped with nickel filtered Cu Kα radiation source operated at 40 kV and 40 mA. The basal spacing or d_{001} reflection of the samples was calculated from Bragg's equation by monitoring the diffraction angle 2θ from 2 to 10^o.

J. *Transmission Electron Microscope (TEM)*

The morphology of the nanocomposites was observed using a JEOL JEM electron microscope with an accelerating voltage of 100 kV. Ultrathin specimens of 100 nm thickness were cut from the middle section of the compression molded bar using a Leica ultra microtome. The specimens were collected on a trough filled with water and placed on a 200 mesh grid.

Table I
Composition, Parameters and Modification of HDPE/EPDM and HDPE/EPDM filled OMMT

Systems	Matrix	OMMT content (vol%)	Surface modification
Control	HDPE/EPDM	-	-
Control-50 kGy	HDPE/EPDM	-	Electron beam irradiation at 50 kGy
Control-100 kGy	HDPE/EPDM	-	Electron beam irradiation at 100 kGy
Control-150 kGY	HDPE/EPDM	-	Electron beam irradiation at 150 kGy
Control-200 kGy	HDPE/EPDM	-	Electron beam irradiation at 200 kGy
Control/OMMT	HDPE/EPDM	2, 4, 6 and 8	-
50 kGy/OMMT	HDPE/EPDM	2, 4, 6 and 8	Electron beam irradiation at 50 kGy
100 kGy/OMMT	HDPE/EPDM	2, 4, 6 and 8	Electron beam irradiation at 100 kGy
150 kGy/OMMT	HDPE/EPDM	2, 4, 6 and 8	Electron beam irradiation at 150 kGy
200 kGy/OMMT	HDPE/EPDM	2, 4, 6 and 8	Electron beam irradiation at 200 kGy

Control system= uncrosslinked or untreated system; OMMT= organophilic montmorillonite; HDPE= high density polyethylene; EPDM= ethylene propylene diene monomer

IV. RESULTS AND DISCUSSION

K. *Tensile strength and modulus*

The effect of different clay loading on control and EB irradiated systems is demonstrated in Fig. 1 and Fig. 2. It is observed that, the tensile strength and modulus for all nanocomposite system began to increase up to 4 vol% of OMMT. As clay loading exceeded 4 vol%, the tensile strength and modulus of all system were found to decrease. Similar improvement in tensile strength and modulus were also reported by previous researchers in their work on any polymer/organo clay nanocomposites [1-6]. The primary cause for such improvement was attributed to the better interaction of polymer chains with clays and large number of interacting molecules due to the dispersed phase volume ratio characteristic of largely intercalated and exfoliated clay platelets as evidenced by TEM micrograph.

An increment of 47.14%, 40.24%, 39.84% and 35.74% in tensile strength were observed for EB irradiated system at doses rate of 100, 50, 150 and 200 kGy. On the other hand, 49.54%, 31. 43%, 23.56% and 22.33% improvement in modulus were observed at doses rate of 100, 50, 150 and 200 kGy. The tensile strength and modulus maximized at 18.51 MPa and 701.39 MPa with 4 vol% of OMMT and irradiation dose of 100 kGy. This indicates the formation of radiation induced crosslinking in the rubber and plastic phases as confirmed by the gel content analysis. At higher doses rate, the tensile strength decreased due to the breakdown of the network structure [8, 9]. Evidently, as revealed by XRD and TEM examinations, clay aggregates were easily broken up and uniform dispersion of clay particles can be achieved with the aids of EB irradiation.

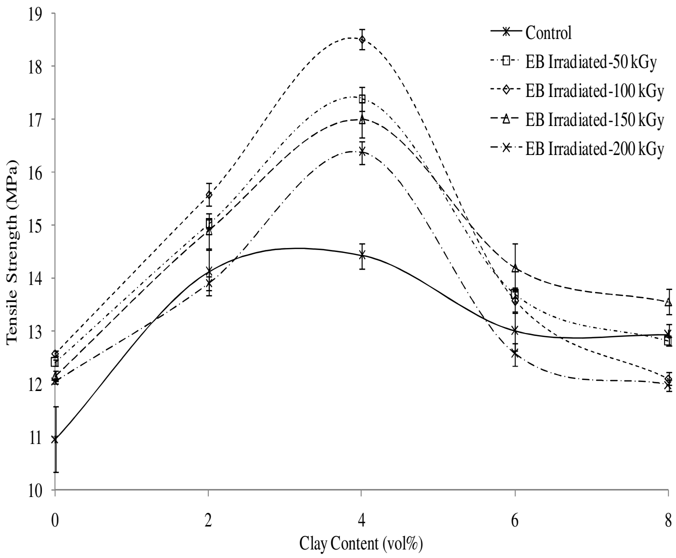

Fig. 1. Tensile strength for control and EB irradiated systems at different clay loadings (vol%) and irradiation doses rate (kGy)

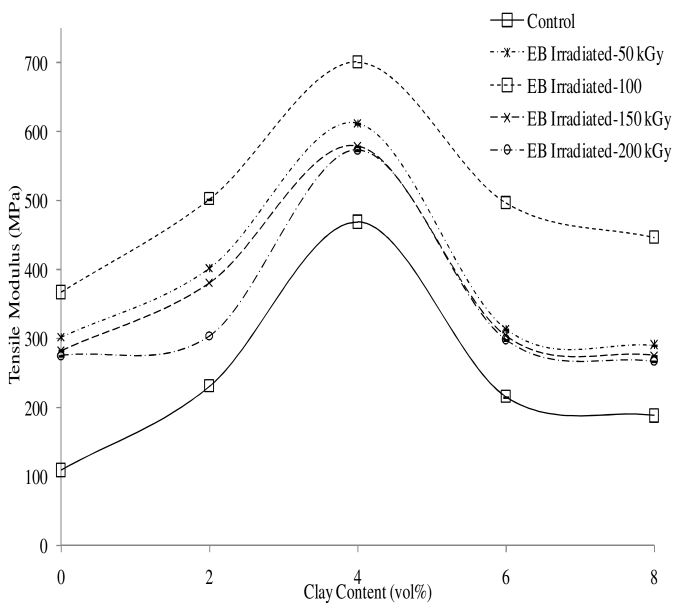

Fig. 2. Tensile modulus for control and EB irradiated systems at different clay loadings (vol%) and irradiation doses rate (kGy)

L. Impact Strength

The effect of clay loading on control and EB irradiated system of notched Izod impact strength is depicted in Fig. 3. It can be seen that a moderate increment on the impact strength for all pristine and nanocomposite system with initial incorporation of 2 vol% OMMT followed by a sudden dropping at 6 vol% of OMMT loading. This is possible due the presence of acceptable amount of rubber compound as impact modifier along with OMMT due to the dispersion of rubber phase as spherical domains in polymer matrix and contributes to improve the toughness. Similar pattern behavior was also reported in previous studies [3-6].

EB irradiated system had obtained the highest value of impact strength as compared to control system. The impact strength of EB irradiated increased with clay loading but decreased as clay loading reached 6 vol% and above. For unfilled composites, an increase of 29.51% is achieved at optimum 100 kGy dose rate followed by 22.96%, 21.63% and 20.01% improvement at 50, 150 and 200 kGy. Moreover, the introduction of 4 vol% OMMT loading enhanced the impact strength by 25.34%, 20.22%, 17.54% and 14.61% at 100, 50, 150 and 200 kGy. This is might be due to the crosslinking effect in pristine composite and nanocomposite systems which resulted in three dimensional and gel-like structures. In contrast, the reduction in impact strength was contributed to the radiation induced scission in which caused the break of carbon-carbon bond.

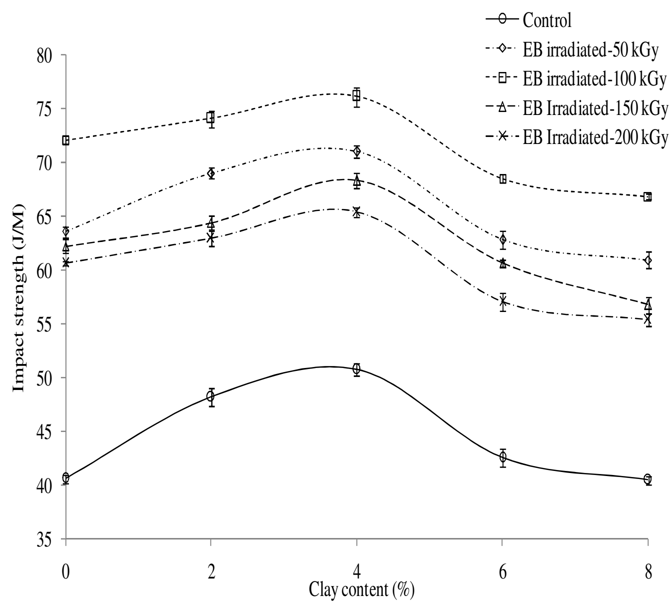

Fig. 3. Impact strength for control and EB irradiated systems at different clay loadings (vol%) and irradiation doses rate (kGy)

M. Gel Content Analysis

The degree of crosslinking for control and EB irradiated systems was estimated from the gel fraction determination. Based on the tensile and impact properties result, the gel content analysis is discussed at optimum OMMT loading of 4 vol%. As evidenced in Fig. 4, there was no gel formation observed for the control system without the addition of OMMT. As 4 vol% of OMMT loading was introduced into the control system, only 20% of gel formation was observed. The gel percentage of pristine composite increased with OMMT loading for both untreated and treated nanocomposites. In this study, the tensile strength property was identified to affect the extent of crosslinking via gel formation. A linear relationship is obtained between the tensile strength and gel formation percentage where higher tensile strength will result in higher gel percentage.

For EB irradiated system, the gel content increased rapidly by increasing the radiation dosage up to 100 kGy, beyond which it slowly decreased. An enhancement of 62.49%, 70.38%, 53.17% and 41.81% was observed for HDPE/EPDM matrix. Moreover, for HDPE/EPDM filled OMMT filler, an improvement of 70.44%, 86.02%, 60.25% and 50.71% was obtained in gel formation. This may be attributed to a better dispersion of nano particles (either partial or fully exfoliated) at 4 vol% of OMMT loading as evidenced in Fig. 7.

As EPDM and HDPE are organic polymers which are categorized radiation crosslinkable materials then such formation of crosslinks upon irradiation are to be expected in them. Kim and Nho (2009) mentioned that the degree of crosslinking increases with irradiation dose rate due to the increase in the concentration of the free radicals. As the crosslinking and the chain scission during irradiation occur simultaneously, the decreasing in gel formation beyond 100 kGy might be attributed to the loosening of the network upon irradiation.

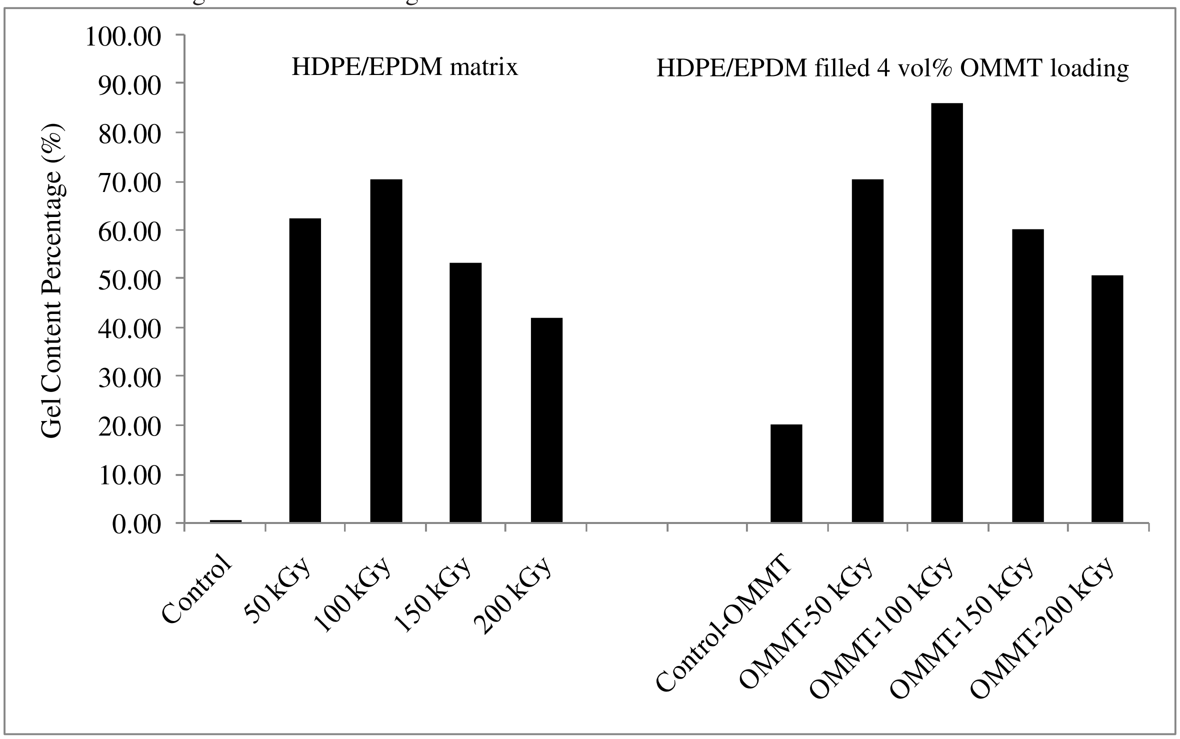

Fig. 4. Gel content formation (%) for control and EB irradiated systems

N. X-Ray Diffraction Analysis (XRD)

The changes in the interlayer distance of OMMT clay can generally be elucidated using XRD. The peak for control system was blunted, indicating that most of the clay is still in the original stacking condition. The diffraction angle and interplanar spacing values are summarized in Table 2.

Nanocomposites with exposure to EB irradiation revealed intercalated with partial exfoliated structure based on the absence of any basal reflections in the XRD patterns. It can be seen from Fig. 5 and Table 2, the diffraction peak was significantly shifted towards lower angle and higher diffraction peak which were about 0.83⁰ and 6.30 Å. This suggested that the face to face interaction between the OMMT particles layers was decreased at the benefit of improving the surface interaction between OMMT particles and polymer matrix. Moreover, this might be implied that the interlayer distance between the OMMT particles have become shrinked due to the formation of crosslinking structure [8]. However, the shift in the diffraction peak to lower 2θ value may not necessary offer evidence for complete exfoliation, it may also indicate the mixed OMMT structure of intercalated and exfoliated structure, which has been confirmed by TEM examination.

Table II
Interplanar spacing and diffraction angle values for control and EB irradiated systems

Systems	2Θ (°)	Interplanar spacing, d (Å)
Control/4 vol% OMMT	3.570	24.73

EB irradiated-100 kGy/4 vol% OMMT	2.845	31.03

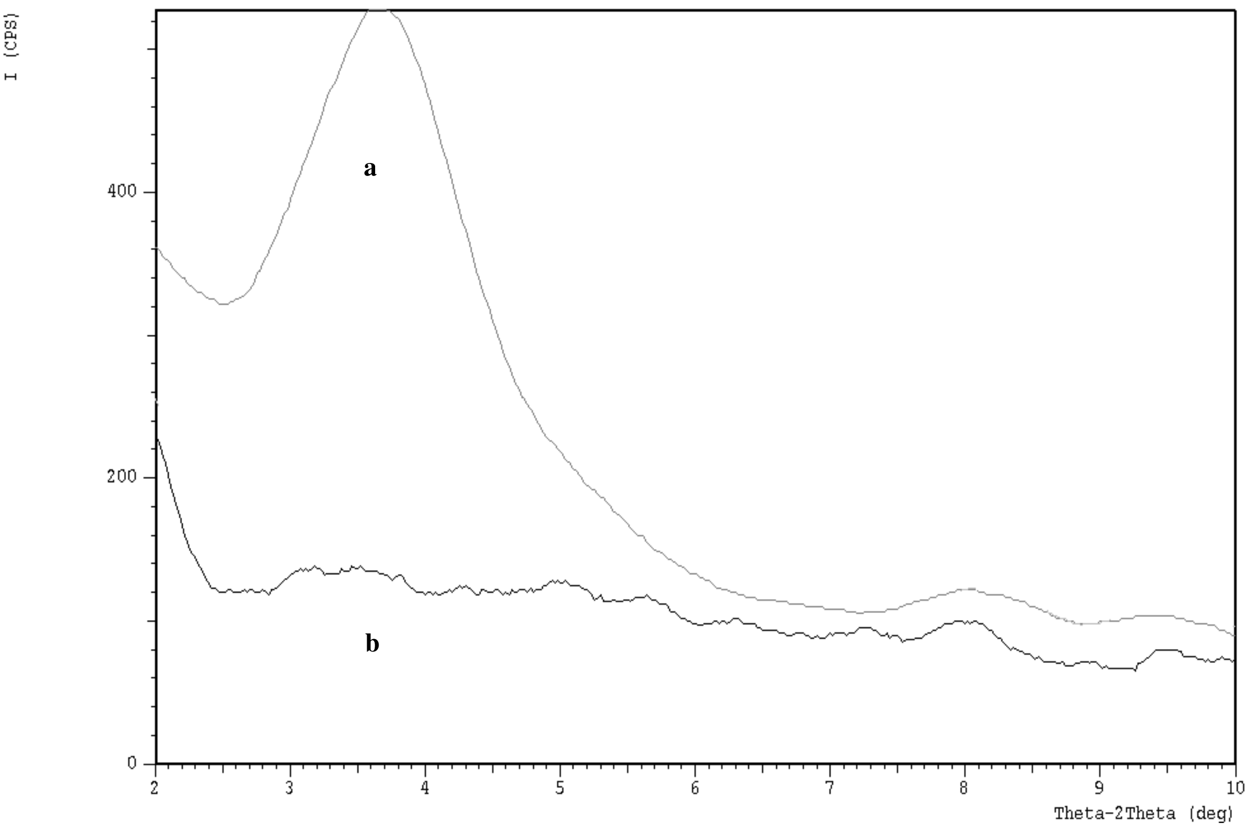

Fig. 5: XRD spectrum for a) control and b) EB irradiated systems

O. Transmission Electron Microscope (TEM)

The nanometer scale dispersion of the treated clays OMMT within the polymer matrix is further corroborated with TEM images as depicted in Fig. 6 and Fig. 7, respectively. The lighter region represents HDPE part, the dark region represents EPDM part whereas the dark electron dense phase corresponding to silicate layers (OMMT).

Individual silicate layers along with two to three layer stacks were found to be intercalated in the polymer matrix for control system as evidence in Fig. 6. In the case of control system, the non-uniform of OMMT agglomerates was easily detected. Moreover, it can be seen that the dispersion of the clay particles was poor and many large aggregates (in microns) were observed.

However, in the case of the EB irradiated system as shown in Fig. 7, partially exfoliated and fine dispersion of the clay layers within the polymer matrix were observed. Modification of clay with high energy EB irradiation lowered the electrostatic interactions between the clay layers enlarged their intra-gallery spacing thus facilitating exfoliation and efficient dispersion of the clay [8, 10, 12]. It is also demonstrated superior nanocomposites performance as discussed in tensile and impact properties part.

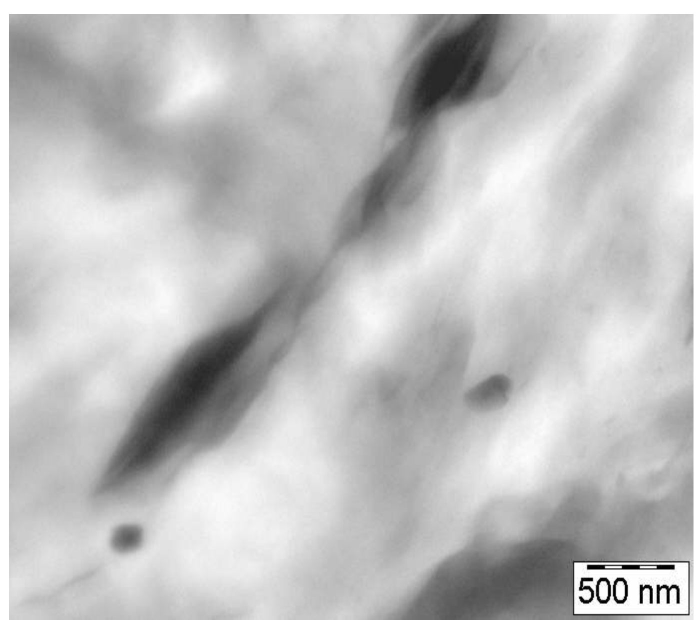

Fig. 6. TEM micrograph of control system (untreated)

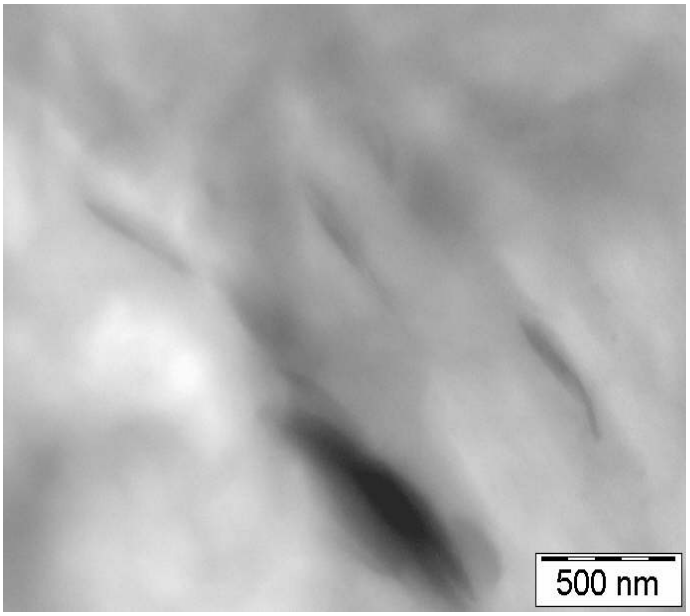

Fig. 7. TEM micrograph of EB irradiated system

V. CONCLUSION

The effects of EB irradiation as crosslinking agent on the mechanical properties and gel content formation of both HDPE/EPDM matrix and HDPE/EPDM filled OMMT systems were investigated in the current study. It is found that a good balance of properties in terms of stiffness and strength was achieved at 4 vol% OMMT content. Moreover, surface modification through electron beam (EB) radiation has induced high crosslinking as evidenced by gel content analysis, thus enhancing the mechanical properties of HDPE/EPDM matrix and HDPE/EPDM filled OMMT systems. High energy EB irradiation can be an alternative as better impact and surface modification of nanocomposites system in which it can replace the role of chemical crosslinking which has been applied in many study for decades.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to University of Malaysia, Perlis, Ministery of Higher Education (MOHE) and International Islamic Malaysia University for the financial assistance and all the staffs in MRB, MINT, SIRIM and IIUM for their help in making this study success.

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