International Journal of Science and Engineering (IJSE)

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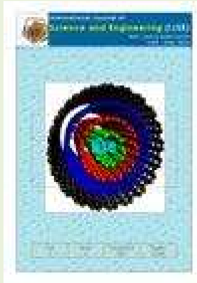

Dynamic Mechanical and Gel Content Properties of Irradiated ENR/PVC blends with TiO_2 Nanofillers

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Abstract - *Numerous studies reported on irradiated epoxidized natural rubber/polyvinyl chloride (ENR/PVC) blends and the blends were found miscible at all compositional range thus it offers a broad of opportunity in modifying the blend characteristic. Addition of low loading titanium dioxide (TiO_2) nanofillers in the ENR/PVC blends has shown a remarkable increment in tensile strength. Thus, this study was initiated to address the effect of TiO_2 nanofillers on ENR/PVC blends dynamic mechanical and gel content properties and its morphology upon exposure to electron beam irradiation. ENR/PVC blends with addition of 0, 2 and 6 phr TiO_2 nanofillers were first blended in a mixing chamber before being irradiated by an electron beam accelerator at different 0-200 kGy irradiation doses. The influence of TiO_2 nanofillers on the irradiation crosslinking of ENR/PVC blends was study based on the dynamic mechanical analysis which was carried out in determining the glass transition temperature and the storage modulus behavior of ENR/PVC blends incorporated with TiO_2 nanofillers. Formations of irradiation crosslinking in the blend were investigated by gel content measurement. While, the TiO_2 nanofillers distribution were examined by Transmission Electron Microscope (TEM). Upon irradiation, the ENR/PVC/6 phr TiO_2 formed the highest value of gel fraction. For dynamic mechanical analysis, it was found that electron beam radiation increased the Tg of all the compositions. The relationship between the crosslinking and the stiffness of the nanocomposites also can be found in this study. The enhancement in the storage modulus and Tg at higher amount of TiO_2 in the blend could be correlated to the enhancement of the irradiation-induced crosslinking in the nanocomposites characteristic and also with the higher agglomerations of TiO_2 evidence shown from the TEM micrograph examination. Lastly, the dimensions of TiO_2 in the blends were found less than 100 nm in diameter which indicates incorporation of TiO_2 nanofillers in ENR/PVC blends is potentially to provide the nanocomposites features.*

Key words - *TiO_2 nanofillers, irradiated ENR/PVC, electron beam radiation, nanocomposites.*

Submission: September 14, 2013 Corrected : November 9, 2013 Accepted: November 12, 2013

Doi: 10.12777/ijse.6.1.24-30

[How to cite this article: Ramlee, N.A., Ratnam, C.T., Alias, N.H[1], Rahman, M.F.A.. 2014. Dynamic Mechanical and Gel Content Properties of Irradiated ENR/PVC blends with TiO_2 Nanofillers. International Journal of **Science** and **Engineering**, 6(1),24-30. Doi: 10.12777/ijse.6.1.24-30]

Introduction

Several studies on irradiated ENR/PVC blends had proved that these blends are miscible at all compositional range and thus offers a great interest in preparing an engineering composite material use such in medical devices manufacturing and automotive industry. Polymer composite systems have a large scale for industry or research area due to the light weight, design flexibility and process robustness characteristics. Incorporation of fillers create an alternative approaches in developing a new polymer composites with better performances due to their outstanding mechanical properties. In attempt to improve the mechanical strength of the polymer blend, nanocomposite inorganic filler become commercially available.

Nanocomposite fillers where the particle size tends to be <100 nm is seen to be emerging as a replacement for the conventional fillers. They are effective as reinforcing fillers at lower concentrations and are therefore cheaper to use. In addition, in early studies some nanocomposite fillers appear to impart antioxidant effects, photostability, and flame retardant to the composite [1]. Filler distribution affects the properties of the blend, as it is controlled by the molecular weight of the polymer and filler dispersion in each phase and chemical interaction between polymer and filler [2]. Some researcher verified that the use of fillers can significantly affect the UV-induced degradation of a polymer material [3-7]; for instance, in rigid PVC compounds, it is the titanium dioxide (TiO_2) added to the formulation that is responsible for its UV resistance and its outdoor lifetime.

TiO_2 is an inorganic particles and it presents special features such as self cleaning, photovoltaic, anti bacterial and UV protector offers tremendous improvement in performance properties of the polymer matrix. In year 2005, Kamisli and Turan [8] has found that additional of TiO_2 in PVC composition has reduced the effective depth penetration of ultraviolet light into the surface of an article formed from such a composition. On the other part, study on mechanical strength of irradiated ENR/PVC incorporation at lower loading of 2 phr TiO_2 nanofillers has been carried out and the scientific outomes revealed that high tensile strength were performed at the highest irradiation exposure [9] on the polymer matrix.

Thus, this present study extends to look into the dynamic mechanical analysis, gel content and the distribution of TiO_2 nanofillers at different exposure of radiation dose and varies of TiO_2 nanofillers loading. The effects of 2 and 6 phr TiO_2 nanofillers addition via melt blending technique on dynamic mechanical analysis and morphological properties of 50/50 ENR/PVC blends were investigated. The properties of the ENR/PVC incorporated with TiO_2 nanofillers which were irradiated at different dose rate in range of 0–200 kGy were also discussed.

Materials and Methods

A. Materials

Epoxidised natural rubber, grade "Epoxyprene 50" with 50 % epoxidation level was obtained from Malaysian Rubber Board (MRB), polyvinyl chloride (PVC) with a <Mn> of 66,000, grade "MH66,6519" was purchased from Industrial Resin (M) Ltd. The Tin stabilizer which issued to stabilizer the PVC, was purchased from Polymer Resources Sdn. Bhd. They were used as received. The TiO_2 investigated in this study was supplied by the Sigma Aldricha and its diameter less than 100 nm.

B. Blending Preparation

Melt blending was carried out at 150 ^oC and 50 rpm rotor speed with a Brabender Plastograph W50 E-3 Zones. The blending was prepared as shown in Table 1. ENR-50 was charged into the mixing chamber for 1 minute before it was added with PVC compound. After 5 minutes of blending, TiO_2 was charged into the mixer. The mixing was continued for another 5 minutes. The blends obtained from the Brabender Plastograph were compression molded into 1 mm thick sheets under a pressure of 130 bars at 160 ^oC for 3 minutes. The sheets were immediately cooled between two plates of a cold press.

C. Blending Radiation

The molded sheets were irradiated using a 3 MeV electron beam accelerator at a dose range of 0-200 kGy. The acceleration energy, beam current, and dose rate are 3 MeV, 5 mA, and 50 kGy/pass, respectively.

D. Characterization of ENR/PVC/TiO_2 nanocomposites

Upon radiation, irradiated ENR/PVC/TiO_2 samples were then characterized based on the gel content measurement, dynamic mechanical analysis (DMA), and transmission electron microscope (TEM) examination.

1. Measurement of Gel Content

Gel content measurement represents the crosslink density of polymer in which the higher the value of gel content the higher amount of crosslinking in the polymer. The gel content of the crosslinked samples was determined by the extraction of samples in tetrahydrofuran (THF) solvent at 50 ± 2 ^oC. The samples were extracted with solvent THF for 24 hours and the extracted samples were dried till constant weight. The gel fraction is calculated as:

$$\% \text{ Gel content} = (W/Wo) \times 100 \tag{1}$$

Where, W and Wo are the weights of the dried samples after extraction and the weight of the sample before extraction, respectively.

2. Dynamic Mechanical Analysis

In order to determine the glass transition temperature (Tg) and modulus behavior, dynamic mechanical analysis (DMA) was performed using Perkin-Elmer DMA-7e in the temperature/time scan mode with a parallel plate attachment. The measurements were carried out at a heating rate of 10 ^oC/min over a temperature range of -100 to 100 ^oC and a frequency of 1 Hz.

3. Transmission Electron Microscopy (TEM)

Samples were characterized by transmission electron microscopy (TEM) using Jeol-JEM-2100 TEM. Macroscopic level analyses of each of component blends were examined at 15000x, 20000x and 40000x magnification.

Table 1. ENR/PVC/TiO_2 blend compositions

ENR	50	50	50
PVC	50	50	50
TiO_2	0	2	6

Results and Discussion

1. Gel Content Measurement

The effect of irradiation dose rate on the gel content measurement of ENR/PVC blends with addition of TiO_2 nanofillers are shown in Figure 1. It is clearly showed the gel content of the all compositions increased with the addition of TiO_2 nanofillers loading and upon exposure of all blends to the higher irradiation dose rate. The gel content of blends with the presence of 6 phr TiO_2 nanofillers is much higher compared to the blends of 2 phr TiO_2 nanofillers loading. Higher degree of crosslinking are expected to achieved for 6 phr TiO_2 nanofillers loading since its present will further enhance the irradiation-induced crosslinking in the ENR/PVC matrix. As mentioned by Friedrich *et al.* [10], inorganic particles are well known to enhance the properties of polymer.

Apart from that, the highest gel content was obtained when all compositions were exposed to irradiation dose rate of 200 kGy. Thus, this shows an increase in gel content with the irradiation induced is an indication of formation of crosslinking in the blends. However the increment of the gel content of all compositions is less remarkable when the compositions exposed to high irradiation effect. This is due to the crosslinking and scission effects [11] that might occur in the ENR/PVC matrix when it was being exposed to the high dose rate.

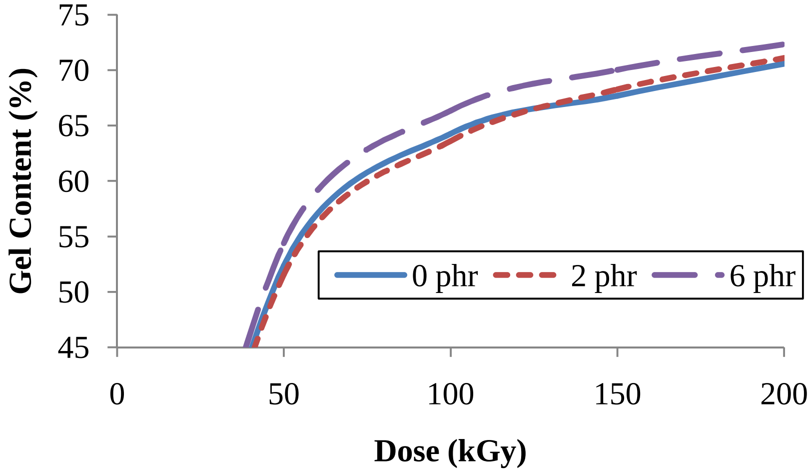

Figure 1. Gel content of irradiated ENR/PVC blends with addition of 0, 2 and 6 phr TiO_2 nanofillers.

2. *Dynamic Mechanical Analysis*

Tan Delta (δ)

Tan delta (δ) is a measure of the ratio of dissipated energy as heat to the maximum energy stored in the material during one cycle of oscillation. From Figure 2.-Figure 4., tan δ values of irradiated ENR/PVC blends with addition of 0, 2 and 6 phr TiO_2 nanofillers were varied and it increased upon 200 kGy radiation effect and also with addition of higher loading of TiO_2 nanofillers. At higher loading of 6 phr TiO_2 nanofillers, the nanofillers presence reduce the composite elastic behavior, caused the elastic system dissipated more energy as heat and forms high tan δ peak.

For all TiO_2 nanofillers loading compositions, it is showed that in the presence of irradiation, sharp tan δ peak were obtained compared to non-irradiated samples. A sharp tan δ peak is clear evidence of high intermolecular interactions with minimum intermolecular chemical heterogeneity in 50/50 ENR/PVC blends [12].

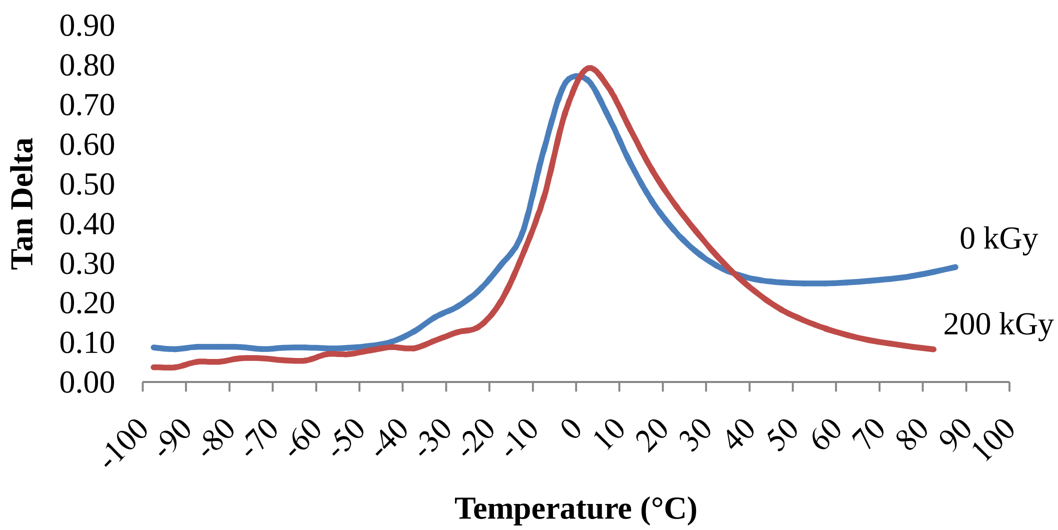

Figure 2. Temperature dependence of tan δ of ENR/PVC/0 phr TiO_2 nanofillers at 0 kGy and 200 kGy radiation dose.

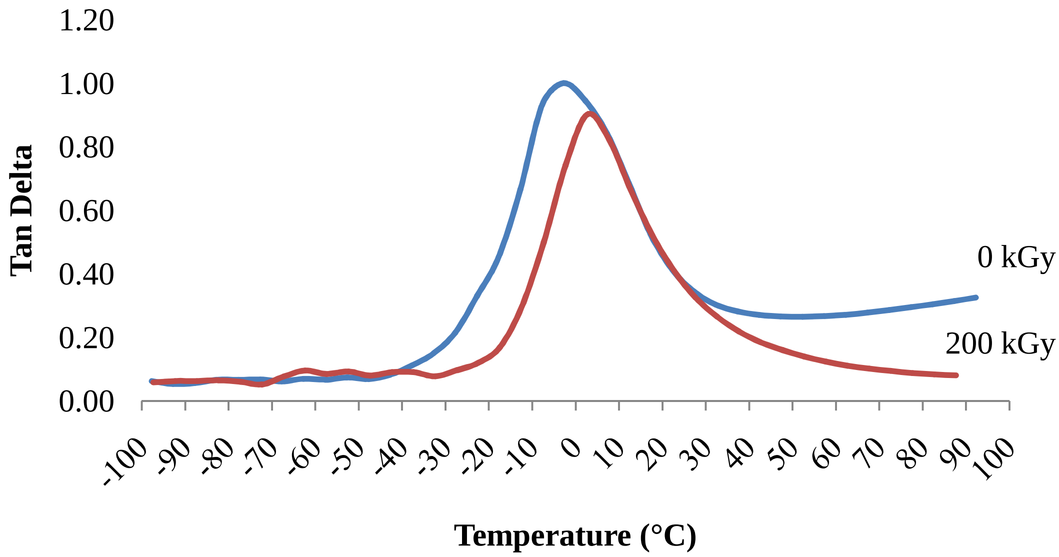

Figure 3. Temperature dependence of tan δ of ENR/PVC/2 phr TiO_2 nanofillers at 0 kGy and 200 kGy radiation dose.

Apart from that, the tan δ curves show the presence of a single peak and this correspondence to irradiated ENR/PVC blends of high miscibility characteristic. The temperature corresponding to the maximum in tan δ is taken as glass transition (Tg) of the blend [13]. Tg of the blend for all compositions is shifted to higher temperature with irradiation. Without irradiation, the ENR/PVC/6 phr TiO_2 nanofillers showed that the temperature at (tan $\delta)_{max}$ is -2.531 °C and it shifted to 2.159 °C upon irradiation of 200 kGy. Similar trend was observed for ENR/PVC blends incorporated with 2 phr TiO_2 nanofillers. While, only slight (tan $\delta)_{max}$ of 2.536 °C to 2.548 °C was obtained for non-irradiated sample. This observation was believed to be associated with the crosslinking induced by the irradiation. As mentioned by Ratnam [14] in the study of PVC/ENR blends, the physical and mechanical properties of the blend could be enhanced by EB radiation.

High tan δ peak and low Tg values obtained for 6 phr TiO_2 nanofillers loading composition (as shown in Figure 4.) and this is believed to be associated with the effect of high amount of TiO_2 introduced in ENR/PVC matrix. Such observation suggests TiO_2 nanofillers provide an ease processing for ENR/PVC melt blending at lower temperature and high amount of this nanofillers in the ENR/PVC blends caused an occurrence of breaker to polymer chain that ruptures the crosslink structure. Meanwhile, Tg of the blend is decreased when too much addition of TiO_2 into the blend due to the occurrence of breaker or mobility to the chain that rupture the crosslink structure. As mentioned by Zoppi *et al.* [15], the degree of crystallinity of the polymeric matrix slightly decreased with the incorporation of an amorphous inorganic phase, TiO_2 into copolymer between polyamide-6 and poly (ethylene oxide).

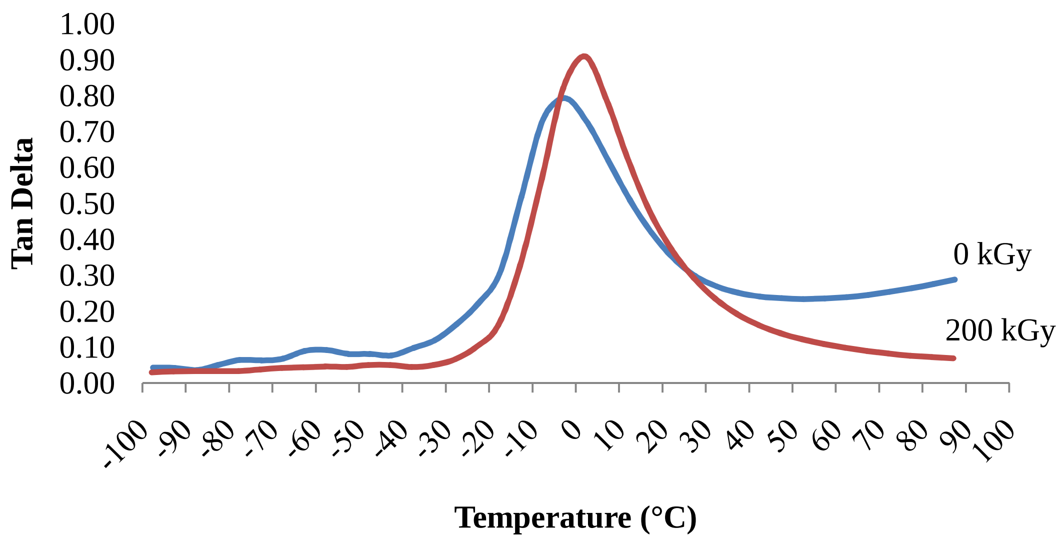

Figure 4. Temperature dependence of tan δ of ENR/PVC/6 phr TiO_2 nanofillers at 0 kGy and 200 kGy radiation dose.

Storage Modulus

The change in storage modulus of all compositions upon irradiation of 0 kGy and 200 kGy is presented in Figure 5. and Figure 6. Storage modulus represents the stiffness of the irradiated blends. Thus, it is obviously illustrated the highest storage modulus was obtained from ENR/PVC/6 phr TiO_2 nanofillers samples irradiated at 0 kGy and 200 kGy. The increase of storage modulus is significant at low temperature. Exposure to 200 kGy irradiation has induced the crosslinking in the ENR/PVC blends thus improved the storage modulus performance of ENR/PVC/0 phr TiO_2 nanofillers. In addition, incorporation of higher nanofillers loading has further increased the stiffness of the composites by transferring the stiffness characteristic of TiO_2 nanofillers to the ENR/PVC matrix as shown in Figure 6. Similar trends were reported by Esthappan [16] when TiO_2 nanofillers has been introduced in single polypropylene matrix in which provided efficient stress transfer between the polymer matrix and TiO_2. Due to poor degree of crosslinked, low storage modulus of non-irradiated samples with 0 phr TiO_2 nanofillers loading is expected since the composition has shown poor gel content properties results.

Nevertheless, at 6 phr TiO_2 nanofillers loading, it is clearly seen that there is no significant differences in the storage modulus upon irradiation of 0 kGy and 200 kGy. Drop in the storage modulus values of ENR/PVC/2phr TiO_2 nanofillers were observed and this may be due to low loading of TiO_2 nanofillers and also the exposure of samples to high dose rate caused high scission or crosslinking effect on the ENR/PVC polymer crosslinking [17] which support the above findings.

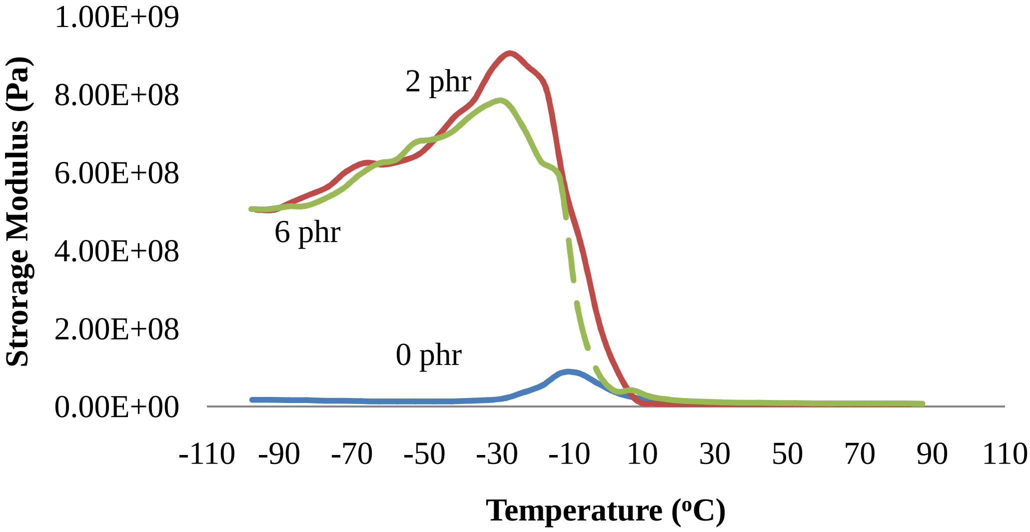

Figure 5. The temperature dependence of storage modulus of ENR/PVC with TiO_2 nanofillers loading at 0 kGy radiation dose.

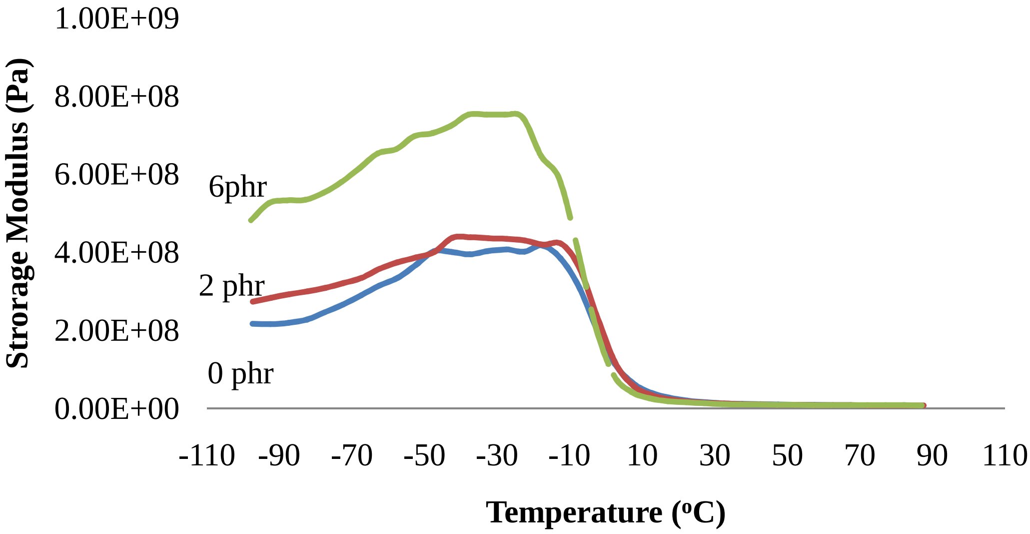

Figure 6. The temperature dependence of storage modulus of ENR/PVC with TiO_2 nanofillers addition at 200 kGy radiation dose.

3. Dispersion of TiO_2 Nanoparticles

Figure 7. illustrates the TEM micrographs for ENR/PVC/2 phr TiO_2 and ENR/PVC/6 phr TiO_2 which the samples have been exposed at different dose rate including 0 kGy, 100 kGy and 200 kGy radiation doses respectively. The lighter region represents ENR/PVC blends matrix while dark region represents the distribution of TiO_2 nanofillers. Distribution and the presence of TiO_2 nanofillers in the ENR/PVC blends matrix were found increased upon to the higher loading of the TiO_2 nanofillers and these observation are expected to be attained since at 6 phr of loading caused a lower Tg results.

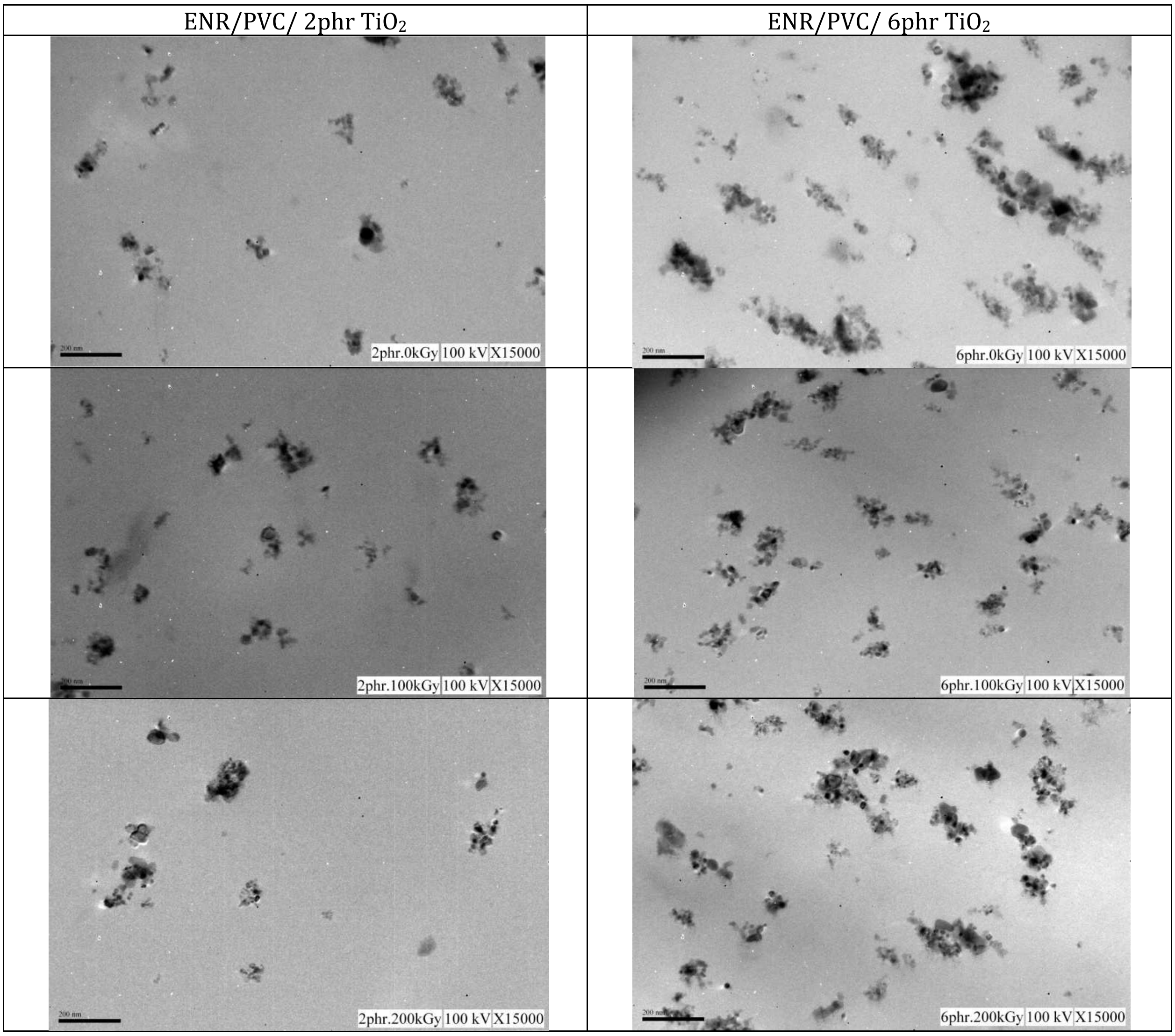

Figure 7. TEM micrograph with addition of 2 phr and 6 phr of TiO_2 into ENR/PVC-50 blend (15000X) at 100 kGy and 200 kGy of radiation dose.

Conclusions

Upon irradiation, the ENR/PVC/6 phr TiO_2 formed the highest value of gel fraction. For dynamic mechanical analysis, it was found that electron beam radiation increased the Tg of all the compositions. The relationship between the crosslinking and the stiffness of the nanocomposites also can be found in this study. The enhancement in the storage modulus and Tg at higher amount of TiO_2 in the blend could be correlated to the enhancement of the irradiation-induced crosslinking in the nanocomposites characteristic and also with the higher agglomerations of TiO_2 evidence shown from the TEM micrograph examination. Lastly, the dimensions of TiO_2 in the blends were found less than 100 nm in diameter which indicates incorporation of TiO_2 nanofillers in ENR/PVC blends is potentially to provide the nanocomposites features.

Acknowledgements

The authors acknowledge the Universiti Teknologi Mara (UiTM) for granting the Excellence Fund (600-RMI/DANA 5/3/RIF (132/2012) to carry out this project. Special thank to Malaysia Nuclear Agency for the expertise, equipment and technical assistance in carrying out the experiments.

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