Effect of Pre-Irradiation of Waste Tire Dust on the Properties of Ethylene Vinyl Acetate/Waste Tire Dust Blend (EVA/WTD) Blends

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Abstract: The effect of pre-irradiation of waste tire dust on the properties and compatibility of ethylene vinyl acetate/ waste tire dust (EVA/WTD) blend was investigated. WTD of 80 mesh particle size was irradiated by gamma ray from Cobalt 60 source at doses of 200kGy, 400kGy, 600kGy, 800kGy and 1000kGy. The irradiated WTD was then melt blended with EVA by using a Haake mixer at 50 rpm, 140°C for 10 minutes. All the samples were tested for elongation at break (Eb), tensile strength (Ts), hardness, impact strength, morphological and dynamic mechanical properties. Interestingly, an upward trend was observed for Ts, Eb and hardness of the EVA/WTD blends with irradiation dose. However, the impact strength did not show similar increase with irradiation dose. It was evident from the dynamic mechanical analysis that the compatibility between WTD and EVA was improved upon pre-irradiation of WTD. Photomicrographs obtained from the transmission and scanning electron microscopy were found to support this contention. The decrease in impact strength which counterbalanced by an increase in Eb of EVA/WTD blends revealed the devulcanization of WTD upon gamma irradiation.

Keywords: Waste tire dust (WTD), ethylene vinyl acetate (EVA), irradiation, compatibility, properties.

INTRODUCTION

Scrap tires are valuable and viable resource; the challenge today is to find best way to utilize them in a wide range of applications. Since tires are made of vulcanised rubbers which do not decompose easily, disposable of scrap tires is a serious environmental problem. Development of technologies for recycling waste tires, which are acceptable from the environmental standpoint, and cost-effective, has proven to be a difficult challenge due to complexities inherent in the reuse of tires. Establishing optimal processes for the reuse/recycling of scrap tires thus remains a worldwide challenge as we enter the new century. The inherent problems associated with the recycling of rubber products have resulted in the development of various methods to reuse elastomers. Attempts to recycle rubber for redesigning in its primary function include reclaiming, oxidative decoupling of rubber scrap [1], ultrasonic depolymerisation of rubber scrap [2], the use of microwave [3] and combination of biological and microwave treatment [4].

One of the promising alternatives to utilize waste tire rubber is the preparation of thermoplastics elastomers. Scrap rubber, namely waste tire dust, WTD can be blended with thermoplastics such as ethylene vinyl acetate (EVA) to produce thermoplastic elastomers (TPEs) with a range of properties. Besides having physical properties of both, thermoplastics and elastomer and processability similar to that of thermoplastics; TPEs provides better material utilization, as scrap and rejects can be recycled. Replacement of TPEs virgin components with recycled polymers is very important from economic and ecological standpoints. Unfortunately, direct introduction of WTD into recipes of different polyolefin/rubber TPEs results in a significant decrease in their tensile properties due to the poor interfacial adhesion between the blend components [5-9]. As an approach to overcome this problem, researchers incorporated a number of different modification techniques such as recycle rubber particle size reduction, varying compatibilizing techniques [5, 10, 11] and performing oxidation treatments on the surface of waste rubber [12]. However, to date, no attempts have been made to study the effect of pre irradiation of WTD on the compatibility and mechanical properties of EVA/WTD blends. This paper reports the effect of gamma irradiation of WTD on the mechanical properties and compatibility of EVA/WTD blends.

MATERIALS AND METHODS

Material

Ethylene-vinyl acetate, EVA (Grade H2020) having 15% vinyl acetate content with melt flow index (MFI)

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E-ISSN: 2311-8717/14

value of 1.5 g/10 min and density of 0.93 g/cm^3 was purchased from the Polyolefin Company, Singapore. Rubber dust from recycle tires (80 mesh) used in this study was obtained from Sin Rubtech Consultancy Sdn.Bhd.

Gamma Irradiation

Gamma irradiation of WTD were performed by JS 10000 IR219 (Nordian), using a 2 x 10 ^{6}Ci ^{60}Co source. WTD powder was exposed to 200, 400, 600, 800 and 1000 kGy irradiation doses at 22.37Gray/min, under air atmosphere.

Blend Preparations

The EVA/WTD blends of different blend ratios (100/0,90/10,80/20,70/30,60/40) were prepared by melt-mixing the EVA and WTD in a Haake Rheomix Polydrive R600/610 at 140°C and 50 rpm rotor speed for 10 min. .The blending was done as follows:

When the desired temperature was reached, EVA was charged into the mixing chamber and allowed to melt for 2 min. Then the irradiated WTD was added to the molten EVA and the mixing was continued for another 8 min. The blends from the Haake Rheomix were then compression moulded into 1 mm thick sheets under a pressure of 14.7 MPa at 123°C for 5 min. The sheets were immediately cooled between two plates of a cold press at 25°C. Similar preparation method was followed for the preparation of neat EVA (0 parts of WTD)

Tensile Properties

The tensile properties were measured with Instron Universal Testing Machine 4301 H119 at 50 mm/min crosshead speed. The moulded sheets of 1mm thickness were cut into dumb bell shaped test pieces using BS6746 die. Seven samples were used for tensile tests and average results were taken as the resultant value.

Hardness

Hardness test specimens were directly compression moulded according to ASTM D2240 Type Shore A samples. The test piece had a length of 100 mm, width of 100 mm and thickness of 5mm. Testing was conducted at room temperature using hardness tester with blunt indenter (Durometer Hardness model Zwick 7206). A minimum of 9 hardness readings were recorded for each sample and average results were taken as the resultant value.

Impact Strength

The Izod impact test was performed at liquid temperature using a 4 joule hammer on notched samples by a Universal Digital Pendulum Model CEAST machine in accordance to ASTM D 256-97. A total of seven samples were used for the impact test and an average of five results was taken as the resultant value.

Dynamic Mechanical Analysis

Dynamic mechanical properties were measured with Perkin Elmer, dynamic mechanical analyzer DMA 7e. The experiment was conducted in a 3 point bending mode at a frequency of 1 Hz. The temperature was increased at 5 °C/min over the range of -80 °C to 80 °C. The dimensions of the samples were approximately 1 mm thick, 10 mm length and 10 mm width.

Transmission Electron Microscopy (TEM)

80/20 EVA/WTD blends (0 and 800kGy) were characterized by transmission electron microscope on carbon coated copper grid in Jeol-JEM-2100 TEM. Ultrathin sections with thickness approximately 80 nm were cut with Leica Ultracut UCT ultra microtome cooled to -100 °C using liquid nitrogen and placed on to a copper grid. Later, the samples were observed under transmission electron microscope using a voltage of 200 kV.

Scanning Electron Microscopy (SEM)

SEM observations were made on the cryogenically fractured surfaces of the 80/20 EVA/WTD samples before and after irradiation (800kGy). The fractured surfaces were then sputter coated with gold and examined using Scanning Electron Microscope model Zeiss SUPRA 35VP

RESULTS AND DISCUSSION

The effect of pre-irradiation of WTD on the tensile strength (Ts), elongation at break (Eb) and hardness of EVA are shown in Figures **1**, **2** and **3** respectively. It is obvious from Figures **1** to **3** that prior to pre irradiation of WTD, a deterioration in Ts, Eb and hardness of EVA has occurred upon incorporation of WTD. The decline in the physical properties of EVA upon addition of WTD is attributed to the poor compatibility of EVA with WTD [7, 8]. Such a drop in Ts and hardness can also be explained through a volume rate of additivity where the higher strength EVA molecules are gradually replaced by the lower strength of WTD phase. This trend of

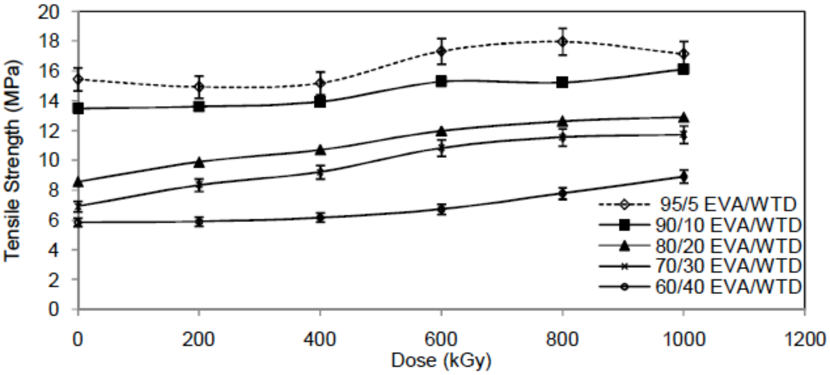

Figure 1: Effect of pre irradiation of WTD on the Ts of EVA/WTD blends.

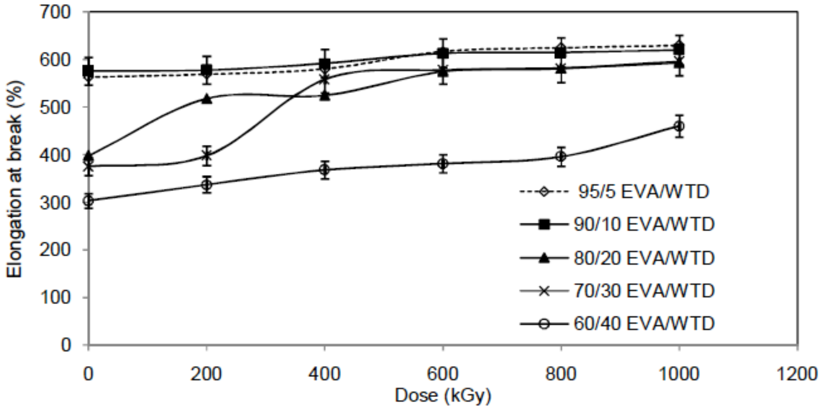

Figure 2: Effect of pre irradiation of WTD on the Eb of EVA/WTD blends.

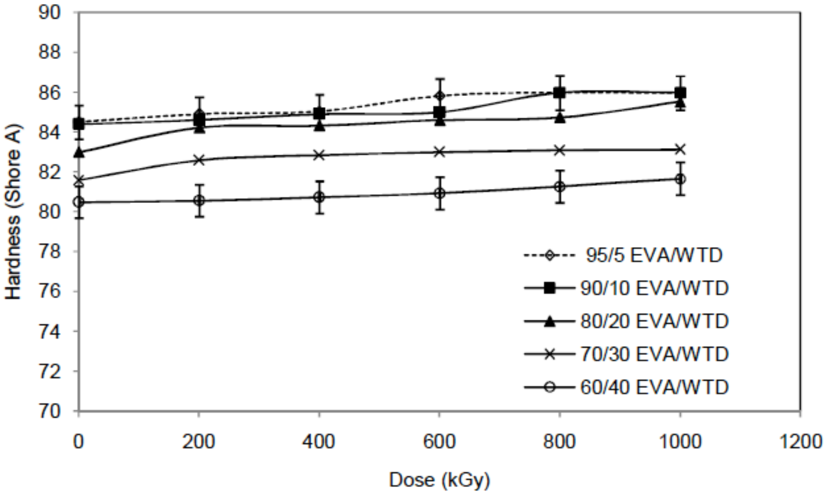

Figure 3: Effect of pre irradiation of WTD on the hardness of EVA/WTD blends.

results also associated with the poor distribution of WTD particle in EVA phase which promote a high particle-particle interaction among WTD to form agglomerates. Formation of such agglomerates will lower the ability of the blend to resist stress. The similar observation was also noted by Awang and Ismail [13] for PP/WTD blends. Besides this, the reduction in Eb with the addition of WTD can be associated with the reduction in chain mobility of the EVA with the inclusion of WTD which serve as filler in EVA matrix.

Figures **1**, **2** and **3** also show a progressive increase in the Ts, Eb and hardness of EVA/WTD blend with gamma irradiation dose, implying property enhancement has occurred upon pre-irradiation of WTD. Such enhancement in the mechanical properties believed to be attributed by the improvement in the compatibility between WTD and EVA upon pre-irradiation of WTD. High energy radiation has the ability to produce reactive cations, anions and free radicals in polymeric material. These reactive free radicals, cations and anions can result in crosslinking, chain branching and chain scission [14]. During irradiation in the presence of air, some of the polymeric radicals, which would otherwise form crosslinking, react with oxygen to form peroxidic structures, which eventually decompose and cause oxidative degradation of the main chain. When rubbers are exposed to radiation in the absence of radiation sensitizers, chain scission dominates over crosslinking [15]. Thus, during irradiation of WTD, the rubber molecule and crosslinked three-dimensional network structure can be broken down through radiation induced chain scissioning which would results in reduction of molecular weight of rubber chain. Evidences on the breakdown of network structure of polymers to a smaller network (microgel) upon irradiation can be found in literature [16, 17]. Smaller molecular weight rubber fragments can increase the homogeneity and interfacial interaction between the polymers during melt blending which will lead to increase in the compatibility of the blends [18, 19].

Figure **4** depicts the effect of pre-irradiation of WTD on the impact strength of EVA. As observed for Ts, Eb and hardness the addition of WTD found to cause a decrease in impact strength of EVA. The poor wetting of the WTD by the EVA will lead to poor interfacial adhesion between the WTD and polymer matrix resulting in weak interfacial regions. Thus, the reduction in impact strength of EVA with the addition of WTD is believed to be due to the agglomeration of the WTD particles to form a domain that acts like a foreign body as well as weak interfacial region between EVA and WTD. However the impact energy found to behave differently with irradiation dose. The impact strength of 5/95 and 10/90 EVA/WTD blends exhibit an increase until it reaches a maximum at 400kGy and show a decline thereafter. The initial increase in impact strength of the blends is attributed to the increase in the compatibility of the blend upon irradiation of WTD similar to Ts, Eb and hardness discussed in the previous section. However, in contrast, impact strength found to show a downward trend at higher irradiation doses. Such decline in impact strength with irradiation dose is associated with the reduction in the elasticising effect of the WTD particles due to the breakdown of three dimensional networks. This observation has been attributed to the reduction in crosslink density of WTD with the radiation-induced chain scissoning which would result in reduction in elasticity of the WTD.

Generally an elastomer should represent a system as elastic as possible to absorb more energy. Toughening effect of elastomers [20] are reported to increase by dynamic vulcanization of plastic/rubber blends. Optimum particle size, good interfacial bonding as well soft and flexible rubber is required for effective toughening. Thus the drop in impact strength suggests the occurrence of devulcanisation of WTD which had occurred during gamma irradiation of WTD. The increase in Eb observed with irradiation dose further supports this contentation. It should be highlighted that for blends loaded with above 10 parts of WTD, the impact strength found to show a gradual drop with irradiation dose. This observation implies that at higher WTD loading, the agglomeration of WTD found to influence the properties over the increase in the compatibility of the blend. Furthermore, the reduction in toughening effect due to breakdown of the crosslinked network found to be more prominent at higher WTD loading. Therefore, it is appropriate to infer that the

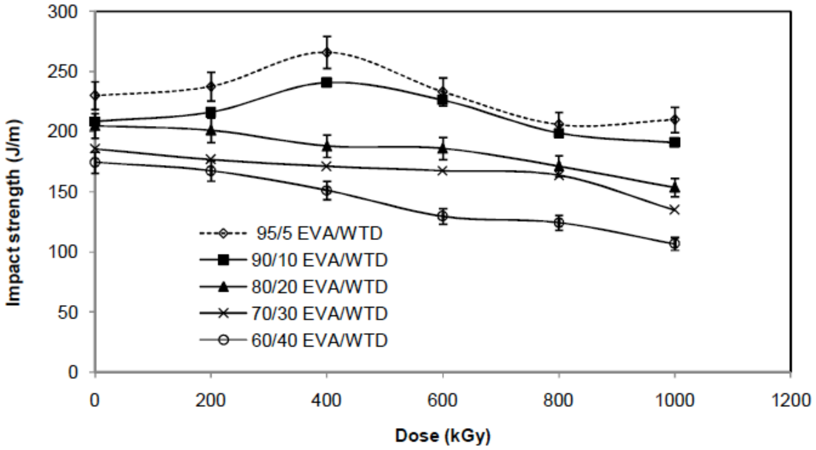

Figure 4: Effect of pre irradiation of WTD on the impact strength of EVA/WTD blends

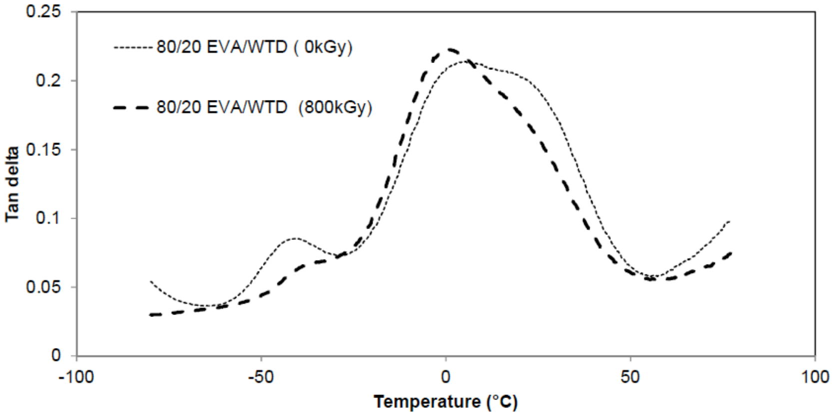

Figure 5: Effect of pre irradiation of WTD on the temperature dependence of the tan δ of 80/20 EVA/WTD blend.

decline in impact strength of EVA/WTD blend is attributed to the agglomeration of WTD particles and radiation devulcanisation of WTD.

Figure **5** shows tan delta curves of 80/20 EVA/WTD blends before and after 800kGy irradiation. Here the temperature corresponding to tan δ maxima (tan δmax) is taken as the glass transition temperature, Tg. From Figure **5**, it is obvious that two peaks are significant for EVA/WTD blends, the temperature of the first peak which corresponds to the Tg of WTD while the second peak corresponding to Tg of EVA, can be noted. Thus, it is evident that prior to irradiation the EVA/WTD blends are incompatible. However upon irradiation at 800kGy the peak corresponds to the Tg of WTD found to exhibit a tendency to disappear and formation of a single peak is observed. The presence of a single tan δ peak in DMA results is an indication of a homogeneous single phase or good dispersion [20-22]. Thus, it is evident that improvement in the compatibility between WTD and EVA is achieved upon irradiation of the WTD.

The morphology of 80/20 EVA/WTD blends before and after pre-irradiation of WTD were studied by TEM and depicted in Figure **6**. It is apparent from Figure **6** that the EVA/WTD blend made up of dispersed WTD particles (darker phase) in a continuous EVA matrix. The well-defined boundaries between WTD particles and the smooth shaped WTD particles prior to irradiation denote poor compatibility and low adhesion between WTD and EVA. However, for EVA/ WTD blend in which WTD was irradiated at 800kGy, the individual primary WTD particles cannot be distinguished, the shape of WTD are not regular and less distinct interfaces are observed. This observation indicates that a better compatibility between EVA and WTD had been achieved upon irradiation of WTD. This change in the morphology of EVA/WTD blend upon irradiation of WTD could also be responsible for the reduction in impact strength since the morphology is amongst other factors which controls the amount of energy absorbed.

Figure **7** shows the SEM micrographs of 80/20 EVA/WTD before and after irradiation of WTD at 800 kGy. The fractured surface of the unirradiated blend shows a smooth failure surface, indicating that lower energy required to break the sample compared to the

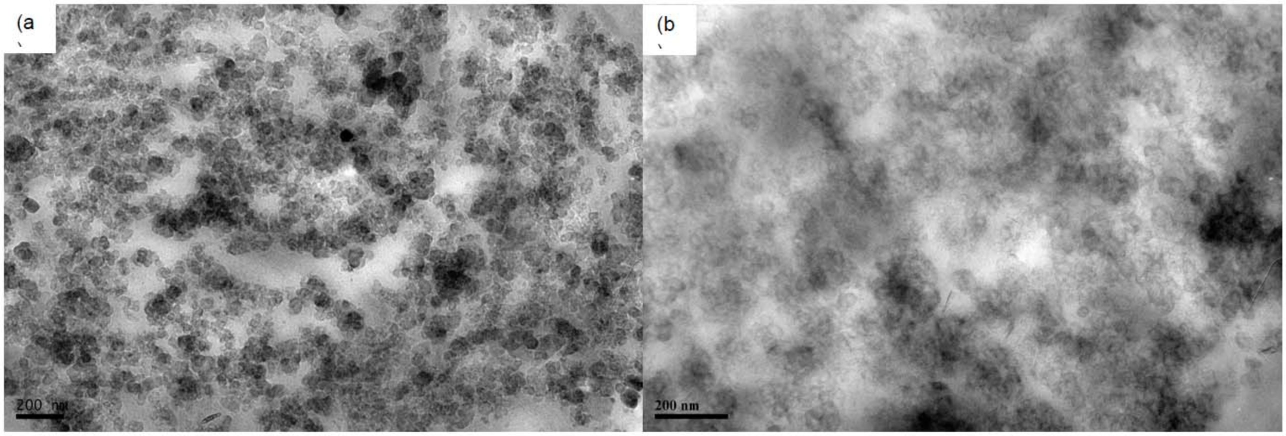

Figure 6: TEM image of80/20 EVA/WTD blends. (**a**) 0kGy (**b**) 800kGy (magnification x15,000).

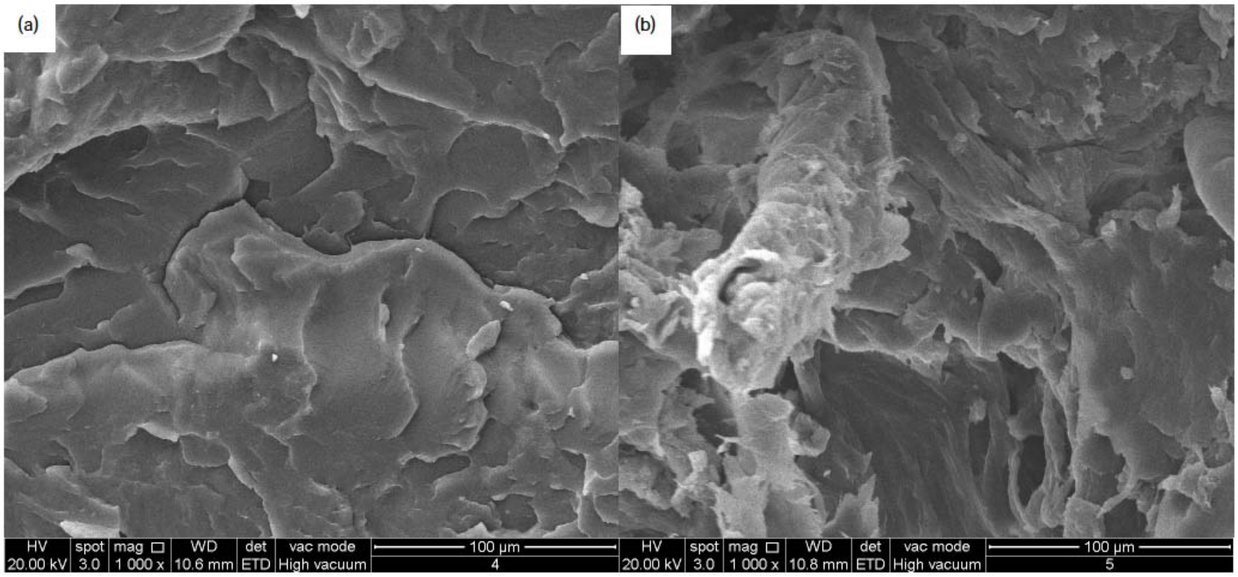

Figure 7: SEM photomicrographs of 80/20 EVA/WTD blend (**a**) 0kGy (**b**) 800 kGy (magnification x1000).

irradiated EVA/WTD blend. The fracture surfaces of the irradiated blend appear to be more ductile with a presence of deformed cavity compared to the unirradiated one. The fracture paths are elongated and deeply penetrated into the material. The material found to stretch longer before failure with fibrous pullout indicating occurrence of plastic deformation. Such changes in fractured surfaces upon irradiation are attributed to the increased in interfacial adhesion between EVA and WTD. These effects could account for the enhancement in measured Ts, Eb and hardness. The presence of fibrils on the fracture surface of irradiated EVA/WTD blend reflects the decrease in the elasticity of the blend upon irradiation due to breakdown of crosslinked network. This observation resembles well with the results on Eb and impact strength discussed in previous sections.

CONCLUSION

The Ts, Eb and hardness of the EVA/WTD blend found increase with gamma irradiation dose. This observation has been attributed to the improved compatibility of the blend upon pre irradiation of WTD. From the discussion of the results, it reveals that the compatibilization of EVA/WTD through pre-irradiation of WTD involves radiation-induced chain scissions which lead to break down of crosslinked network in WTD. The enhancement in the compatibility of EVA/WTD blend upon pre-irradiation of WTD was confirmed from the dynamic mechanical analysis and morphological examination of EVA/WTD blends. The progressive increase in Eb with simultaneous decrease in impact strength of EVA/WTD blend with irradiation dose further revealed the devulcanization of WTD upon gamma irradiation.

ACKNOWLEDGEMENT

The authors wish to thank all Nuclear Malaysia's gamma irradiation facility (MINTEC SINAGAMA) staff, Mr Wan Ali and Mr Falah of Nuclear Malaysia for the assistance during the irradiation and laboratory facility usage. The financial support from Ministry of Education Malaysia (MOE) under Fundamental Research Grant Scheme (FRGS/1/2012/TK04/IP-ANM/04/1) is kindly acknowledged.

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Received on 25-11-2013 Accepted on 10-12-2013 Published on 25-12-2013

DOI: http://dx.doi.org/10.12974/2311-8717.2013.01.01.3