

COMPATIBILIZATION OF WASTE TIRE RUBBER/POLY(ETHYLENE-CO-VINYL ACETATE) BLENDS USING LIQUID RUBBER AND ELECTRON BEAM IRRADIATION.

Rubber Recycling

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Abstract

Accumulation of rubber waste is a pressing global issue. Tires are complex bulky rubber composite which has received global recycling attention. At the end of life, tires are collected, shredded, segregated, ground and down-sized into rubber recyclates, more commonly known as waste tire rubber. These waste tire rubber, having undergone a lifetime on the road and downsizing processes, has poor properties and is not favored in high-end applications. Many researchers have attempted to blend waste tire rubber with plastic to produce thermoplastic elastomer. However, one of the most prominent drawbacks of these thermoplastic elastomers was the poor interfacial adhesion which results in poor mechanical properties. In this study, the above mentioned problem was addressed by blending 50 wt% of reclaimed waste tire rubber (WTR) with 50 wt% of poly(ethylene-co-vinyl acetate) (EVA) which was compatibilized using liquid styrene-butadiene rubber (LR). Compatibilized blends were prepared using an internal mixer. The blends were later subjected to electron beam irradiation with doses ranging from 50 to 200 kGy. While compatibilization on its own did not distinctly enhance the properties of the blends, the irradiation remarkably enhances mechanical and dynamic mechanical properties of the blend by at least 2 folds compared to un-irradiated blends.

1. INTRODUCTION

The world is consuming finite resources, and producing vast quantities of products as well as waste, leading to unsustainable patterns of consumption and production. It is essential to move away from the traditional linear “make, use and dispose” economy, to a circular model. A circular economy is defined as an economic system aimed at minimising waste and making the most of resources [1]. This regenerative approach is in contrast to the traditional linear economy [2]. In order to achieve this, intense planning of the entire lifecycle of a manufactured product, which involves the production, utilisation and retirement phases, is essential [3]. The rubber industry is one of the many industries facing the problem in establishing circular economy due to lack in successful recycling motives [4].

Tires are the major consumer of raw rubber and has a short lifetime. At the end of tire life, an estimated 67% of material is recyclable and reusable [5]. Tire making industries has been investing many different approaches to achieve circular economy. However, recycling tire rubber has been a difficult process due to the complex structure and mixture of materials [6]. Tires need to be shredded, segregated and granulated before it can be converted into ground tire rubber (GTR). This can be processed further with the use of chemicals to obtain reclaimed tire rubber (RTR) [7].

Having undergone a life on road, post life processing and chemical treatments; GTR and RTR has very poor properties and are not fit to be converted to other useful products as it is. Hence, many has tried incorporating GTR and RTR into thermoplastics such as PP and PE to formulate a new thermoplastic elastomer [8]. However, one of the major setback was the poor properties resulting from the lack of interfacial adhesion [9].

Alternative methods such as irradiation on tire rubber based thermoplastic elastomers blends has been heavily reported [10]. The results are varied from positive to negative enhancements in many different properties. Exposure to irradiation such as gamma ray and electron beam can induce crosslink and chain-scission within the polymer matrix. The dominance of either process will influence the resulting properties of the blends.

In this study, attempt was made to compatibilize RTR and ethylene vinyl acetate (EVA) blend using liquid rubber and electron beam irradiation. The aim was to enhance the interfacial adhesion and thereby enhancing the mechanical and dynamic properties.

2. METHODOLOGY

In this section, the materials and methods used to conduct the work is presented.

2.1. Materials

Poly(ethylene-co-vinyl acetate) (Grade EVA N8045), EVA, having 18% vinyl acetate content with melt flow index value of 2.3 g/10 min and a density of 0.947 g/cm³ was purchased from the TPI POLENA Public Limited Company, Thailand. Reclaimed tire rubber (RECLAIM Rubberplas C), RTR, from waste, heavy duty tires used in this study was supplied by Rubplast Sdn. Bhd., Malaysia. General properties of the RTR are 48% rubber hydrocarbon, 5% ash content, 15% acetone extract, 25% carbon black fillers and density of 1.3 g/cm³. The styrene butadiene based liquid rubber (LR) supplied by Kuraray Co. Ltd. Japan had a density of 0.95 g/cm³; molecular weight of 8500 and glass transition temperature of -14 °C.

2.2. Compounding and compression molding

EVA, RTR and LR were melt blended in an internal mixer (Brabender Plasticoder PL2000-6 equipped with co-rotating blades and a mixing head with a volumetric capacity of 69 cm³). The rotor speed was set at 50 rpm while blending temperature was set at 120 °C.

EVA was fed into the internal mixer chamber and allowed to melt for two minutes, followed by the addition of RTR and LR. EVA, RTR and LR were allowed to mix for 8 minutes before collecting the blends from the internal mixer. LR loading was set at 1, 3, 5 and 10% based on rubber weight. The control blend (without compatibilizer) was set at 50 wt% RTR and 50 wt% EVA and designated as 50RTR. The compatibilized blends were designated as 1LR, 3LR, 5LR and 10LR with the number corresponding to the loading of LR.

2.3. Compounding and compression molding

The compounded materials collected from internal mixer were placed in a mould for compression molding in between the platens of an automated hydraulic heated press (LP-S-50 Scientific Hot and Cold Press). The platens were pre-heated to 130 °C. The molding cycles involve 3 minutes of preheating without pressure to melt the materials; followed by 20 seconds of pressure cycling between 0 to 10 MPa to distribute the melted material in the cavity and dislodge any air bubbles; and 3 minutes of holding pressure at 10 MPa.

Following the holding time, cooling procedure was imposed by carefully removing the mould from the heated press to the adjacent cooling press equipped with water circulating channels pumped with chilled (20 °C) water. Cooling procedure was done for 2 minutes under 10 MPa holding pressure to eliminate non-uniform cooling and warping of the slabs. The cooling rate of the mould was estimated to be between 40 to 50 °C/min. The slabs are then carefully removed from the mould cavity and excess/flash on the slabs was trimmed with a sharp knife.

2.4. Electron beam irradiation

The molded slabs were irradiated using 3 MeV electron beam accelerator (model NHV-EPS-3000) at doses 50, 100, 150 and 200 kGy. The acceleration energy, beam current and dose rate were 2 MeV, 5 mA, and 50 kGy per pass, respectively.

2.5. Gel content analysis

The gel content of the samples was determined according to ASTM D2765. Approximately 3 mg weighed samples were placed in a stainless-steel wire of 120 mesh size. Three replicates were prepared for each sample. The samples placed in wire mesh were then extracted in boiling Toluene using a Soxhlet apparatus for 24 hours

to dissolve the soluble content. Samples were then collected and dried in an oven at 70 °C until a constant weight is obtained. Gel content was calculated as per Equation 1 below.

$$\text{Gel content (\%)} = (w_1/w_0) \times 100 \quad \text{Equation 1}$$

where, w_0 and w_1 are the dried weight of the sample before and after extraction, respectively.

2.6. Tensile testing

Tensile test specimens were punched out using Wallace die cutter from compression molded slabs. The specimens had a gauge length of 25 mm, width of 6 mm and thickness of 1 mm. Tensile properties measurements were performed at ambient temperature according to ASTM D412 using a computerized tensile tester (Toyoseiki, Japan) with a load cell of 10kN. The crosshead speed was set at 50mm/min for all samples. Data for tensile strength, modulus at 100% elongation and elongation at break were recorded. At least 7 specimens were used for each set of blend and average results were taken as the resultant value. Standard deviation of the results was less than 10%.

2.7. Dynamic mechanical analysis

DMA was performed in dual cantilever mode using a dynamic mechanical analyzer (TA Instrument TA01 DMA 2980). The temperature interval was - 80 to 100 °C with a heating rate of 5 °C/min, using a frequency of 1 Hz. The samples were cut out to the dimension of 60 x 12 x 3 mm from compression molded slabs. The sample dimensions were kept as similar as possible in order to obtain an accurate comparison. Variation of storage modulus, loss modulus and $\tan \delta$ values with temperature were recorded. E' and E'' are defined as storage and loss modulus respectively. Peak of $\tan \delta$ is taken as the glass transition temperature (T_g) of the sample.

3. RESULTS & DISCUSSION

Liquid rubber such as liquid natural rubber has been successfully used as a compatibilizer in thermoplastic elastomer blends [11, 12]. Also, studies utilizing ground tire rubber (GTR) in thermoplastic elastomer observed the encapsulation of GTR by the rubber component and good mechanical properties [13-16]. In this study, low molecular weight liquid styrene butadiene rubber (LR) was used, to improve the adhesion between RTR and EVA. Figure 1 shows the schematic representation of RTR/EVA blend compatibilization by LR. RTR phase is encapsulated by LR, efficiently decreasing the interfacial tension. This improves the dispersion of RTR in EVA matrix. Similar observation was also reported in GTR/LDPE blends compatibilized by elastomers [17]. Furthermore, the free chains of LR can co-mingle with both free devulcanized chains of RTR and EVA matrix, improving the interfacial adhesion. Upon irradiation, both EVA and RTR can be adhered together through formation of crosslinks between these co-mingling chains [18, 19].

Figure 2 below shows the gel content of the blends under the influence of LR loading and irradiation dosage. Generally, the gel content is an estimation of yield of irradiation induced crosslinking. 50RTR shows 23.8% of the gel content prior to irradiation (0kGy), affirming the presence of readily existing crosslinks within its matrix. This gel content is the contribution of existing crosslinked structure within the reclaimed tire rubber. LR compatibilized blends showed slightly higher gel content before irradiation (0 kGy) compared to the control, 50RTR blend. All the blends recorded a proportional increase in gel content with respect to irradiation dose starting from 100 kGy onwards. This indicates that 50RTR blends require a minimum of 100 kGy irradiation dose for net effective crosslinking process to take place. LR compatibilized blends, though had slightly higher gel content before irradiation, resulted in comparable gel content yield to control blend from 100 up to 200 kGy irradiation dose. This clearly shows, LR acted as a physical compatibilizer and did not participate in the chemical crosslinking process of the blends.

Figure 3 shows the influence of LR loading and irradiation dosage on tensile strength and elongation at break of the blends. At 0 kGy, LR compatibilized blends recorded lower tensile strength values compared to control blend. The lower values are attributed to the presence of LR which is a low molecular weight substance. A small decrease in tensile strength was also noticed with increasing LR loadings. Similar observation was also reported on liquid natural rubber compatibilized NR/LLDPE blends and NR/HDPE blends [11, 20]. Dispersion of LR into EVA chains might indeed decrease the crystallinity of the EVA phase resulting in the decreasing trend

of tensile strength with increasing LR loading. Irradiation enhanced the tensile strength of the blends by about 10 to 15% compared to non-irradiated blends. The higher the LR loading the lower the enhancement in tensile strength following irradiation despite gel content analysis indicating similar level of crosslinking happening in all compatibilized blends. This is due to increased amount of low molecular weight LR renders the blend softer leading to premature rupture of the samples.

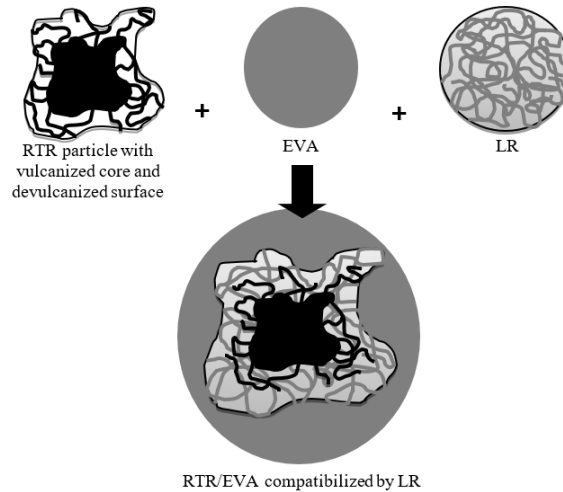


FIG. 1. Representation of physical compatibilization by LR on EVA/RTR blends

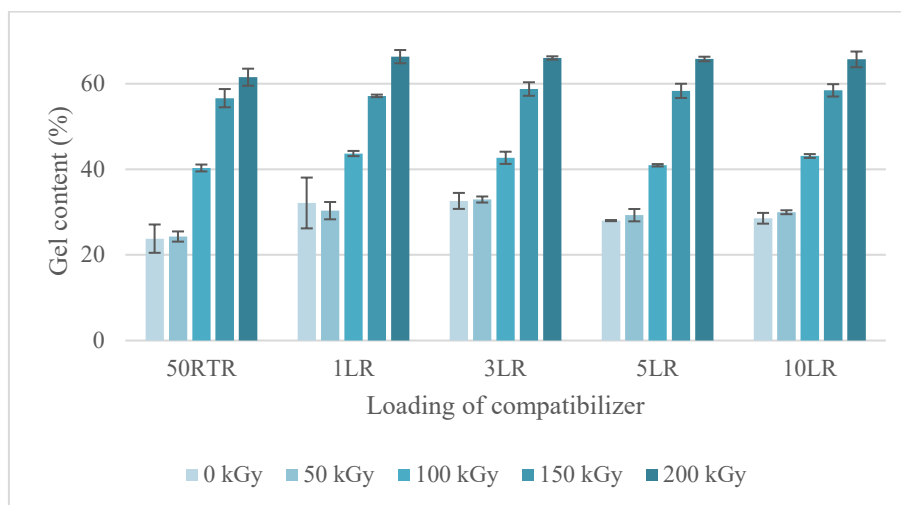


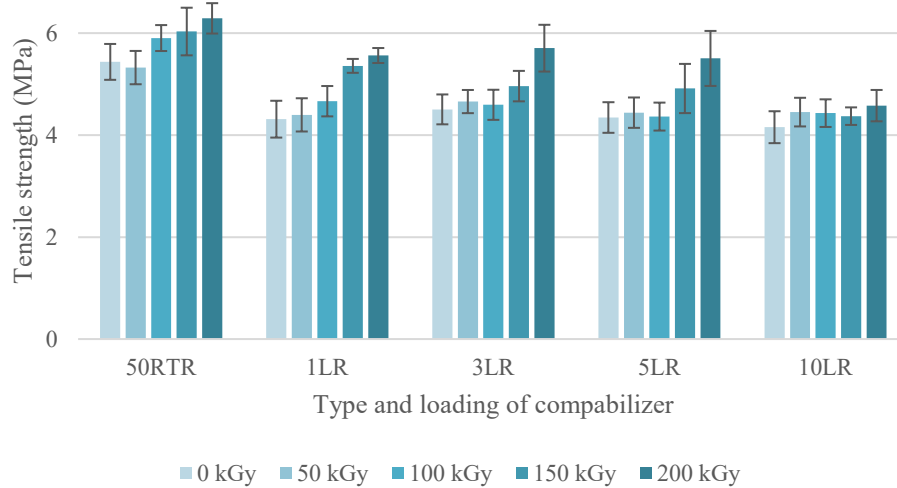
FIG. 2. Influence of LR loading and irradiation on gel content of 50RTR blends.

Figure 3b shows increasing LR loading does not influence the elongation at break of non-irradiated blend. LR is a low molecular weight rubber, which presents itself in the interphase area of RTR/EVA blend, reducing the interfacial tension and improving RTR dispersion, thereby allowing the matrix to elongate a little further before rupture [21]. However, LR also effectively enhances the interfacial adhesion and thereby limits the feasibility of the EVA matrix to elongate. Increasing the irradiation dose, decreases the elongation at break of LR compatibilized blends. Formation of crosslinks induced by irradiation increases the stiffness of the blends resulting in a decrease of elongation at break.

Figures 4 illustrates the storage modulus, loss modulus and tan delta profiles of 50RTR and LR compatibilized blends, before and after 200 kGy irradiation. All the blends, before and after irradiation clearly displayed glass, transition and rubbery characteristics in the storage modulus curve (Figure 4a). Storage modulus was highest in the glassy region and rapidly decreases from transition region and displayed a plateau rubbery curve. Before irradiation, LR compatibilized blend showed decrease in the storage modulus within glass and transition region compared to 50RTR blend.

3LR blend which showed reduction in storage modulus before irradiation (due to plasticizing effect of LR), improved tremendously upon irradiation as the elasticity of the blend increases with efficient crosslink formation in LR. Previous studies have shown an increase in interphase thickness in the presence of compatibilizer [21]. Compatibilizer with higher molecular weight tends to form thicker interphase compared to the fully stretched length of the compatibilizer chain. These findings enhance the fact that presence of an effective compatibilizer restricts the mobility of the matrix chains. Thus, effective compatibilization renders a composite stiffer recording higher storage modulus.

a)



b)

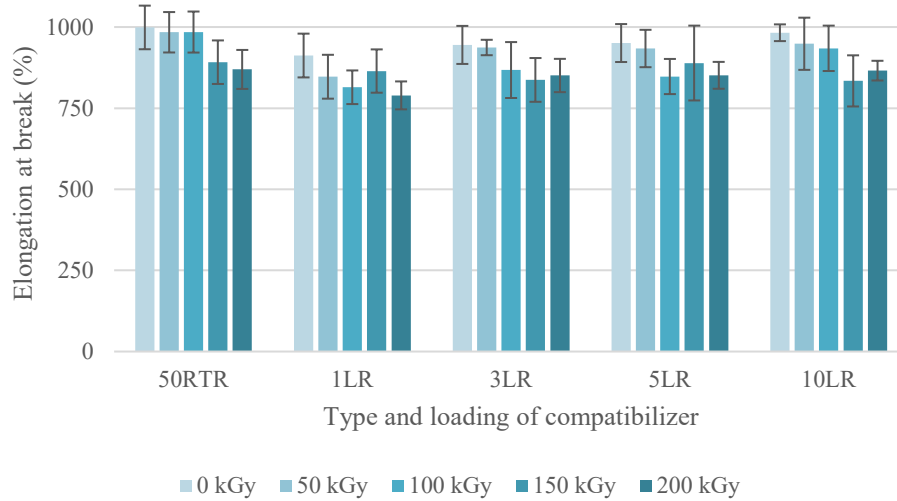


FIG. 3. Influence of LR loading and irradiation on a) tensile strength and b) elongation at break of 50RTR blends.

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Figure 4b shows the loss modulus curve which peaks at the transition temperature range. 3LR compatibilized blends recorded a peak temperature of $-16.8\text{ }^{\circ}\text{C}$, a slight decrease by $3\text{ }^{\circ}\text{C}$, compared to 50RTR. However, no distinct change was observed in the loss modulus peak height. This is again due to physical compatibilizing nature of LR. The slight reduction in loss modulus peak temperature in 3LR compatibilized blend might possibly be due to the contribution of lower T_g values of LR. Interestingly, 3LR compatibilized blend, upon

irradiation, showed shifting of loss modulus peak temperature and height to $-18.2\text{ }^{\circ}\text{C}$ (decreased by $1.4\text{ }^{\circ}\text{C}$) and 374.5 MPa (increased by 140.5 MPa), respectively, compared to non-irradiated counterpart.

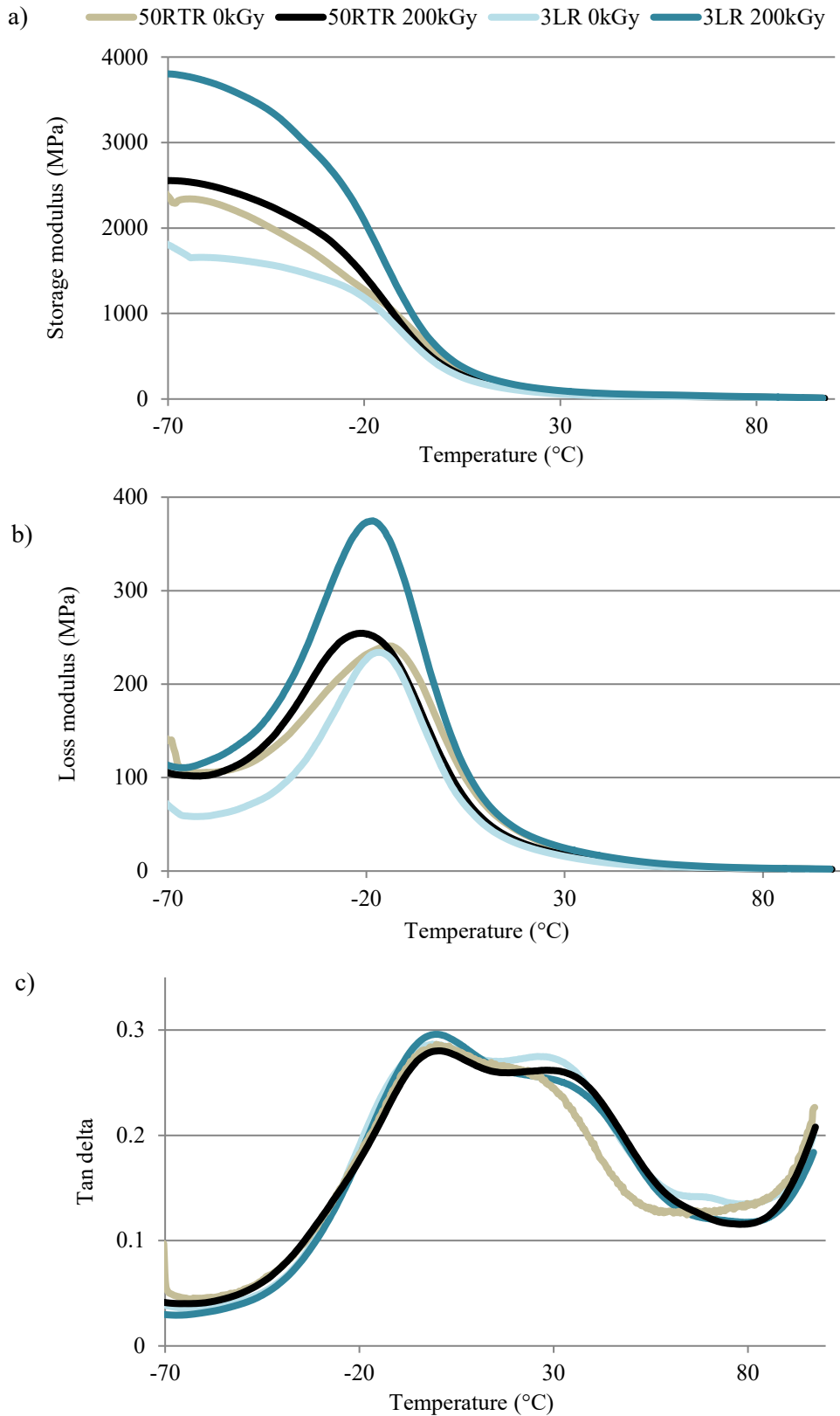


FIG. 4. Influence of LR compatibilization and irradiation on a) storage modulus and b) loss modulus and c) tan delta of 50RTR blends.

Apparently, irradiation induced crosslinking of LR in LR compatibilized blends increases the portion of viscous component in the blend, resulting in increased energy loss in the blend. As compared to irradiated 50RTR, irradiated 3LR blend displayed enhanced loss modulus up to rubbery region (50 °C). This clearly indicates LR have effectively compatibilized the blends and enhanced the dynamic mechanical properties upon irradiation.

Figure 4b shows the loss modulus curve which peaks at the transition temperature range. 3LR compatibilized blends recorded a peak temperature of -16.8 °C, a slight decrease by 3 °C, compared to 50RTR. However, no distinct change was observed in the loss modulus peak height. This is again due to physical compatibilizing nature of LR. The slight reduction in loss modulus peak temperature in 3LR compatibilized blend might possibly be due to the contribution of lower T_g values of LR. Interestingly, 3LR compatibilized blend, upon irradiation, showed shifting of loss modulus peak temperature and height to -18.2 °C (decreased by 1.4 °C) and 374.5 MPa (increased by 140.5 MPa), respectively, compared to non-irradiated counterpart. Apparently, irradiation induced crosslinking of LR in LR compatibilized blends increases the portion of viscous component in the blend, resulting in increased energy loss in the blend. As compared to irradiated 50RTR, irradiated 3LR blend displayed enhanced loss modulus up to rubbery region (50 °C). This clearly indicates LR have effectively compatibilized the blends and enhanced the dynamic mechanical properties upon irradiation.

Tan delta property (Figure 4c) was the least affected by compatibilization and irradiation of 50RTR blend as the peak temperature and height remained around 0 °C and 0.3, respectively. Similar observation was also reported for NBR/EVA blends [22] and PP/NR blends [23]. The breadth of tan delta curve, before irradiation, increased with compatibilization. Compatibilization leads to improved dispersion of RTR in EVA matrix, resulting in increased heterogeneity of the blends. In contrary to 50RTR blend, no increased broadening was observed in the compatibilized blends upon irradiation, suggesting no changes in heterogeneity or presence of side chains in irradiated blends. In a two-phase system, where two polymers are far from being completely miscible, no compatibilizer is likely to change it into one phase system. However, LR compatibilizer acts only as interfacial agents by effectively improving RTR dispersion in EVA, preventing coalescence of RTR particles and reducing interfacial tension [21, 24].

4. CONCLUSION

The study reported on influence of LR compatibilization and electron beam irradiation on enhancing the properties of RTR/EVA blend. Gel content analysis indicated formation of net crosslinking upon irradiation. While tensile strength and elongation barely improved in the presence of LR, irradiation did clearly enhance the said properties. The most prominent enhancement was noted in dynamic mechanical properties of both LR compatibilized and irradiated blends. Hence, LR and irradiation can be used as a mean to enhance the property of 50RTR blend.

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