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Effect of Electron Beam Irradiation on Natural Rubber/Linear Low Density Polyethylene Blends with *m*-Phenylenebismaleimide

(Kesan Sinaran Alur Elektron bersama *m*-Fenilenabismaleimida ke Atas Adunan Getah Asli/Polietilena Linear Berketumpatan Rendah)

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ABSTRACT

The effects of HVA-2 on radiation-induced cross-linkings in 60/40 natural rubber/ linear low density polyethylene (NR/LLDPE) blends was studied. NR/LLDPE was irradiated by using a 3.0 MeV electron beam machine with doses ranging from 0 to 250 kGy. Results showed that under the irradiation employed, the blends NR/LLDPE were cross-linked by the electron beam irradiation. The presence of HVA-2 in the blends caused the optimum dose to decrease and the blends to exhibit higher tensile properties. Further, within the dose range studied, the degradation caused by electron beam irradiation was found to be minimal. The optimized processing conditions were 120°C, 50 rpm rotor speed and 13 min processing time. The gel content, tensile strength, elongation at break, hardness and impact test studies were used to follow the irradiation-induced cross-linkings in the blend. For blends of 60/40 NR/LLDPE with 2.0 phr HVA-2, the optimum tensile strength and dose, were 19 MPa and 100 kGy, respectively. Blends of 60/40 NR/LLDPE without HVA-2, the optimum tensile strength and dose were 17.2 MPa and 200 kGy, respectively.

Keywords: Cross-linking; HVA-2; irradiation; NR/LLDPE

ABSTRAK

Kesan m-fenilenabismaleimida (HVA-2) yang boleh menggalak dan merangsang taut silangan akibat sinaran ke atas adunan getah asli/ polietilena linear berketumpatan rendah (NR/LLDPE) 60/40 telah dikaji. Adunan NR/LLDPE 60/40 disinari pada dos antara 0 dan 250 kGy menggunakan mesin alur elektron 3 MeV. Keputusan menunjukkan bahawa sinaran alur elektron boleh menyebabkan taut silangan dalam adunan NR/LLDPE. Kehadiran HVA-2 dalam adunan NR/LLDPE boleh mengurangkan dos optimum yang diperlukan dan meningkatkan sifat-sifat regangan. Keadaan pemprosesan optimum yang diperoleh adalah suhu 120°C, kadar rotor 50 rpm dan masa pengadunan 13 min. Bagi adunan NR/LLDPE 60/40 yang mengandungi 2.0 phr HVA-2, kekuatan tegasan maksimum dan dos sinaran adalah masing-masing 19 MPa dan 100 kGy. Bagi adunan NR/LLDPE 60/40 tanpa HVA-2, kekuatan tegasan maksimum dan dos sinaran adalah masing-masing 17.2 MPa dan 200 kGy.

Kata kunci: HVA-2; NR/LLDPE; sinaran; taut silangan

INTRODUCTION

The blending of two or more polymers has become an increasingly important technique for improving the cost performance ratio of commercial plastics. For example, blending may be used to reduce the cost of an expensive engineering thermoplastic, to improve the processability of a high-temperature or heat-sensitive thermoplastic, or to improve the impact resistance. Since natural rubber and linear low density polyethylene are not of the same group of polymer, the expected properties will not be achieved because of poor adhesion between the phases created due to immiscibility in the thermodynamics sense. This situation can be remedied by using certain polymers to improve the interfacial interactions between the phases. Some of the compatilizers reported were block co-polymers (Qin et al. 1990) and liquid natural rubber (Ahmad et al. 1994).

The addition of cross-linking agents such as *m*-phenylenebismaleimide (HVA-2) as reported in our previous study, leads to an efficient cross-linkings. The HVA-2 sensitizes the cross-linking reactions and as such a lower absorbed radiation dose is required to generate the required cross-linking density. Consequently, the radiation-induced degradation reactions are reduced and the resulting deterioration of physical properties is avoided (Ivanov et al. 1996). According to Charlesby (1960), natural rubber and polyethylene form cross-links upon irradiation. Therefore, it can increase the gel content and strength of NR/PE. The gel content increases more than 75% when LLDPE is exposed to 200 kGy of radiation dose (Novakovic 1986).

This article discusses the effect of electron beam irradiation on natural rubber/ linear low density polyethylene (NR/LLDPE) blend with and without the presence of HVA-2. The effectiveness of irradiation and HVA-2 in improving the bulk properties of NR/LLDPE blends will be discussed.

EXPERIMENTAL DETAILS

MATERIAL

Natural rubber (NR) of SMR-L grade was purchased from Rubber Research Institute of Malaysia and linear low density polyethylene (LLDPE), Etilinas LL0220SA from Polyethylene Malaysia Sdn. Bhd. HVA-2 was obtained from Trade TCI Mark Tokyo.

BLENDS PREPARATION

Melt blending of 60/40 NR/LLDPE was carried out at 120°C, rotor speed 50 rpm and blending time of 13 min in a Brabender Plasticorder Model PL 2000 mixer with a mixing cam attachment. NR was first discharged into the mixer 3 min before LLDPE. NR and LLDPE were allowed to mix for about 5 min before HVA-2 was added slowly by means of dropping funnel and the blending continue for a further 13 min. The blends obtained from the mixer were then compression molded into 1 mm and 3 mm thick sheet at 170°C for 10 min. The sheets were immediately cooled to 25°C. Dumb-bell shaped test pieces were cut from these sheets in accordance with ASTM D 1822-L.

IRRADIATION

The molded sheets and dumb-bell test pieces were irradiated using a 3 MeV electron beam accelerator at a dose range of 0 – 250 kGy. The acceleration energy, beam current and dose rate were 2 MeV, 1 mA, and 10 kGy/pass, respectively.

GEL CONTENT

The gel content was determined by extraction in toluene, at 50±2°C. The blends were solvent extracted with toluene for 24 h and the extracted samples were dried to constant weight. The gel content was calculated from the weight of dried samples after and before extraction.

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

MEASUREMENT OF MECHANICAL PROPERTIES

The tensile strength and elongation at break were measured on a Toyoseiki model Strograph-RI at a crosshead speed of 50 mm min^{-1}. The samples of 1 mm thickness were cut into dumbbell shape following BS 6746 standard. The hardness of the samples were measured on 3 mm sample thickness using a hardness tester of Shore type A. BS-notched test pieces were prepared and tested using CEAST impact testing at temperatures of -10°C . The measurements were carried out in accordance with ASTM D256. The energy applied was 5.5 J. Five samples were tested and average values were taken.

RESULTS AND DISCUSSION

GEL CONTENT

Figure 1 shows the influence of radiation dose on the gel content of NR/LLDPE 60/40 blends. It was found that the gel content increased when the radiation dose was increased. Dahlan (1998) and Azizan (2004) reported that cross-linking interaction occurred when NR/LLDPE blends were radiated with electron beam. Figure 1 shows that in blends containing 2.0 phr of HVA-2, the gel content increased from 25% to 75% when it was exposed to a radiation dose of 100 kGy. Any further increase of radiation dose does not increase the gel content in the blends. Blends without HVA-2 requires a high dose of radiation in order to achieve maximum gel content compared to the ones that have it. From the results, the gel content of NR/LLDPE clearly showed the effectiveness of HVA-2 as a sensitizer for radiation induced cross-linking. With the presence of HVA-2 in the NR/LLDPE blends, it only required a dose of 100 kGy compared to the ones without HVA-2 which needs 200 kGy to achieve the maximum gel content.

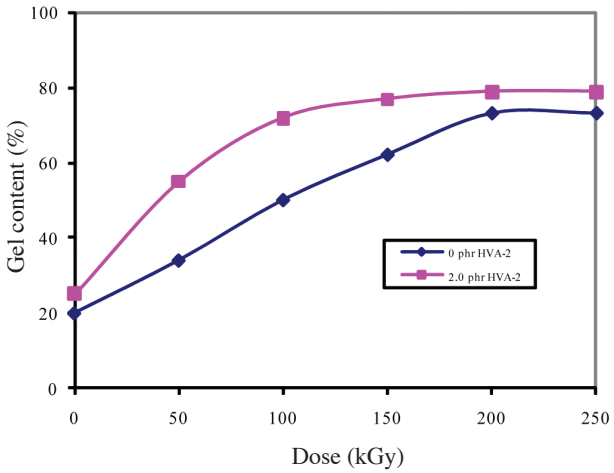

FIGURE 1. Effect of irradiation on gel content

MECHANICAL PROPERTIES

Tabata et al. (1991) reported that the tensile strength of natural rubber increased when radiated to 200 kGy. When NR/LLDPE blends were exposed to radiation, cross-linking occurs rapidly causing the elongation at break to increase. Prolonged irradiation caused the blends to become harder and more brittle. Figure 2 shows the influence of radiation on the tensile strength of NR/LLDPE 60/40 blends. High cross-links density gives a good tensile properties (Jayasuriya et al. 2001). For 2.0 phr HVA-2 blends, the tensile strength increases with the increment of radiation dose until 100 kGy, thereafter further increment only reduced its tensile strength. Increasing radiation dose will increase the degree of cross-linking and high degree

of cross-linking will cause the blend to become hard and brittle, leading to reduction of tensile strength. For 2.0 phr HVA-2 blends, the maximum tensile strength was at 19 MPa at 100 kGy of radiation dose. At higher radiation dose, the cross-links structure will break apart thus reducing the tensile strength. The optimum dose for maximum tensile strength to be achieved was at 100 kGy. According to Vinod et al. (2002), the reduction of tensile strength showed that the chain separation is more dominant in polymer. While for blend without HVA-2, the maximum tensile strength was 17.2 MPa at 200 kGy. Therefore, HVA-2 in this case, can increase the tensile strength and also reduced the dose required to achieve optimum tensile strength. HVA-2 acted as a sensitizer for radiation induced cross-linking in NR/LLDPE blends. Blends with HVA-2 gave better mechanical properties compared to those without.

A lower radiation dose is better for rubber blends since high dose will promote degradation. So, the role of HVA-2 as a as a sensitizer of radiation induced cross-linking is shown in most natural rubber/thermoplastic blends.

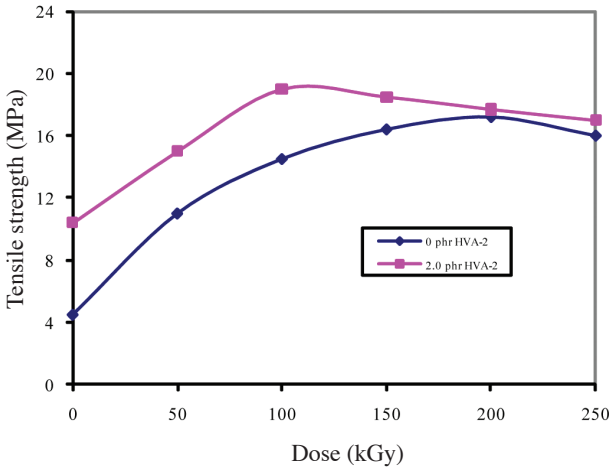

FIGURE 2. Effect of irradiation on tensile strength

Elongation at break indicates the mobility and flexibility of a polymer chain. Figure 3 shows the effect of radiation does on the elongation at break of NR/LLDPE 60/40 blend. The elongation at break of blends without HVA-2 generally increases with every increment of radiation dose, increase from 1032% to 1490% when exposed to dose level of 50 kGy. Afterwards, the elongation at break started to drop. According to Haque et al. (1996), an increase of cross-linking in the rubber phases will cause the elongation at break to decrease. The earlier elongation at break increase (at 50 kGy) was caused by the effect that radiation has on natural rubber and LLDPE. Then, once the dose was above 50 kGy, the elongation at break dropped because the blends' rigidity changes to be more brittle due to the formation of cross-links. Elongation at break is sensitive to any changes of the degree of cross-links. Exposing to radiation caused the blend to become stronger and increases the blends' extensibility property. The extensibility property was at maximum at certain radiation dose but higher dose will only cause this property to decrease. For blends without HVA-2, an increase of radiation dose does not make any significant changes to the elongation at break, in other words, an increase of radiation did not affect elongation at break. For this blend, elongation at break only increased from 1186% to 1232% when exposed to 100 kGy of radiation. According to Ziaie et al. (2005), when elongation at break did not change with radiation increase, it indicated than cross-links had reached saturation point at 100 kGy. Excessive cross-links will stop any rearrangement of polymer molecules structure (Banik & Bhowmick 2000).

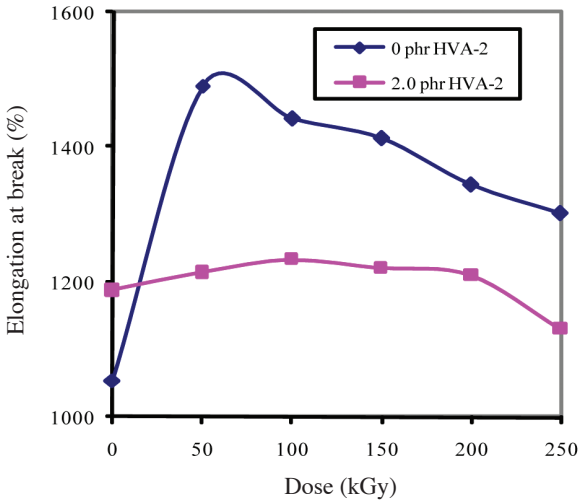

FIGURE 3. Effect of irradiation on elongation at break

According to van Gisbergen et al. (1990), impact strength increment was caused by an increase of adhesion between the components phases caused by radiation induced grafting. While Valenza et al. (1994) reported an increase of impact strength was caused by an increase in the gel content formed in blend. The impact property for NR/LLDPE 60/40 blends is shown in Figure 4. The Izod impact increased with an increase of HVA-2. This shows that the impact strength increases with radiation dose increment up to 100 kGy dose, after which, the impact strength decreases. Increase of impact strength shows that the adhesion between phases also increases (Inoue & Suzuki 1995). The impact strength for blends without HVA-2 was 72 J/m when exposed to 200 kGy of radiation. The presence of HVA-2 with/without radiation can cause the adhesion force between the natural rubber and polyethylene phases to increase that can be seen from the increase of impact strength (Figure 4).

Figure 5 shows the influence of radiation dose on Shore A hardness of NR/LLDPE 60/40 blends. An increase of radiation dose caused Shore A hardness value to increase for both blends. The presence of HVA-2 in the blends caused a higher hardness level compared to those without HVA-2. Thus proving that increment of hardness level in NR/

LLDPE blends was caused by the formation of cross-links, as shown by the gel content. The presence of 2.0 phr HVA-2 in the blends gave a Shore A hardness of NR/LLDPE 60/40 value of 79 at 250 kGy radiation dose. While, without HVA-2 in the blends, Shore A hardness is only 70 when exposed at 250 kGy of radiation dose.

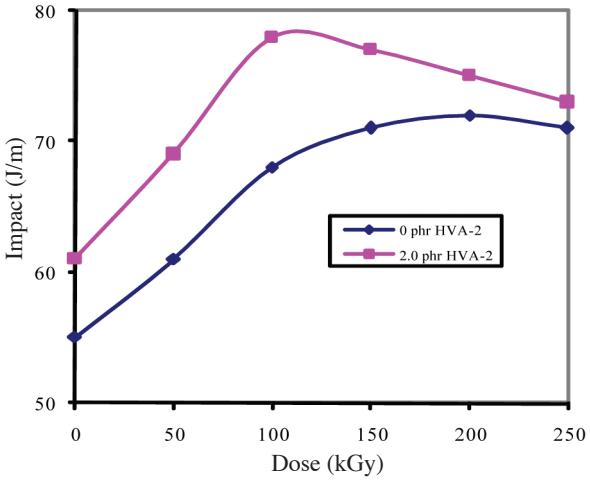

FIGURE 4. Effect of irradiation on impact

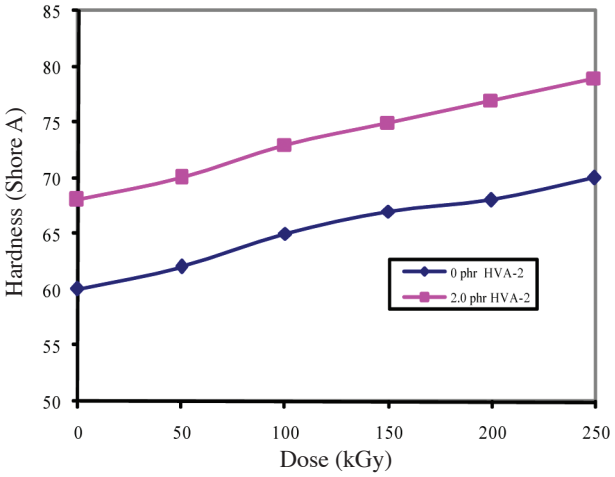

FIGURE 5. Effect of irradiation on hardness

CONCLUSIONS

The HVA-2 sensitizes the crosslinking reactions and as such a lower absorbed radiation dose is required to generate the required crosslinking density. Consequently, the radiation-induced degradation reactions are reduced and the resulting deterioration of physical properties is avoided. The tensile strength increases with increasing dose for the blend, and the optimum tensile strength shifts to a lower dose as the concentration of HVA-2 is increased. The enhancement in hardness of the NR/LLDPE blends was due to the formation of crosslink by radiation. It is expected that the NR/LLDPE becomes increasingly brittle as a consequence of the increasing number of crosslinks as the absorbed dose increases.

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REFERENCES

Ahmad, S., Abdullah, I., Sulaiman, C.S., Kohjiya, S. & Yoon, J.R. 1994. Natural rubber-HDPE blends with liquid natural rubber as a compatibilizer I. Thermal and mechanical properties. *Journal of Applied Polymer Science* 51: 1357-1363.

Azizan Ahmad. 2004. Kesan karbon hitam dan sinaran alur elektron ke atas keserasian adunan getah asli dan polietilena linear adunan getah asli dan polietilena linear berketumpatan rendah. PhD thesis, Universiti Kebangsaan Malaysia, Bangi.

Banik, I. & Bhowmick, A.K. 2000. Effect of electron beam irradiation on the properties of crosslinked rubbers. *Radiation Physics and Chemistry* 58: 293-298.

Charlesby, A. 1960. *Atomic Radiation and Polymers*. Oxford: Pergamon Press.

Dahlan Hj. Mohd. 1998. Peranan getah asli cecair dalam pengserasi adunan getah asli/ polietilena. PhD thesis, Universiti Kebangsaan Malaysia, Bangi.

Haque, M.E., Dafader, N.C., Akhtar, F. & Ahmad, M.U. 1996. Radiation dose required for the vulcanization of natural rubber latex. *Radiation Physics and Chemistry* 48 (4): 505-510.

Inoue, T. & Suzuki, T. 1995. Selective crosslinking in polymer blends III. The effects of the crosslinking of dispersed EPDM particles on the impact of PP/EPDM blends. *Journal of Applied Polymer Science* 56: 1113-1125.

Ivanov, V.S., Migunova, I.I. & Kalina, N.A. 1996. Radiation processing of polymer insulators: A method for improving their properties and performance. *Polymer Engineering & Science* 36(14): 1941-1949.

Jayasuriya, M.M., Makuuchi, K. & Yoshi, F. 2001. Radiation vulcanization of natural rubber latex using TMPTMA and PEA. *European Polymer Journal* 37: 93-98.

Novakovic, L., Markovic, V., Gal, O. & Stannett, V.T. 1986. Themochemical behavior of stabilized PE irradiated with γ -rays. *Rubber Chemistry and Technology* 27: 1-5.

Qin, C., Yin, Y. & Huang, B. 1990. Compatibilization of NR/PE blends by PE-b-PI diblock copolymers. *Polymer* 31: 633-367.

Tabata, Y., Ito, Y. & Tagawa, S. 1991. *CRC Handbook of Radiation Chemistry*. Boca Raton: CRC Press.

Valenza, A., Calderaro, E. & Spadaro, G. 1994. Molecular modification-mechanical behaviour relations for gamma irradiated LLDPE/PA6 blends. *Radiation Physics and Chemistry* 43(4): 315-322.

Van Gisbergen, J., Borgmans, C.P. & van der Sander, M. 1990. Impact behaviour of polystyrene/EPDM-rubber blends: influence of electron beam irradiation. *Polymer Communications* 31: 162-166.

Vinod, V.S., Varghese, S. & Kuriakose, B. 2002. Degradation behaviour of natural rubber-aluminium powder composites: effect of heat, ozon and high energy radiation. *Polymer Degradation and Stability* 72: 405-412.

Ziaie, F., Noori, A., Anvari, F., Ghaffari, M., Ahmadian, V. & Durrani, S. A. 2005. Effect of high dose electron irradiation on specific heat capacity of high impact polystyrene. *Radiation Measurement* 40: 758-761.

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