

Electron Beam Cross-linking of NR/LLDPE Blends

Azizan Ahmad^{1*}, Dahlan Hj. Mohd², and Ibrahim Abdullah³

(1) College of Engineering, Universiti Tenaga Nasional, Kajang-43009, Selangor, Malaysia

(2) Malaysian Institute for Nuclear Technology Research, Bangi, Kajang-43000
Selangor, Malaysia

(3) School of Chemical and Food Sciences, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, Bangi-43600, Malaysia

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ABSTRACT

Effects of electron beam irradiation on the mechanical properties and morphological structure of natural rubber (NR)/linear-low density polyethylene (LLDPE) blend was investigated. The NR/LLDPE blend was prepared by melt blending in a Haake internal mixer at 140°C, rotor speed of 50 rpm, and in 15 min. Liquid natural rubber (LNR) was incorporated into the blend as a compatibilizer. Samples in the form of 1 mm sheets were exposed to 50-300 kGy of electron beam irradiation and analyzed for swelling index and gel content, tensile strength, and surface morphology. The result indicated that gel content and mechanical properties of the samples increased with radiation dosage. The honey-comb structure of the surface morphology in low dosage irradiated samples slowly transformed into a continuous matrix on increasing radiation dose. The variation of mechanical and physical properties was due to increase in cross-linking density in the rubber and plastic phases and rubber-plastic interaction on irradiation.

Key Words:

electron beam;
radiation;
cross-linking;
interaction;
blends.

INTRODUCTION

Natural rubber (NR) and linear-low density polyethylene (LLDPE) are very important industrial elastomer and thermoplastic, respectively which both are widely used in different industries. Thermoplastic properties can be imparted into natural rub-

ber (NR) via its melt blending with any compatible thermoplastic such as polyethylene (PE) or polypropylene (PP). Such blend is generally termed thermoplastic natural rubber (TPNR) and by the physical characteristics exhibited, is categorized as an elas-

(*) To whom correspondence should be addressed.
E-mail: azizan@uniten.edu.my

tomers lying between rubbers and plastics [1]. Structurally, polyethylene is expected to be more readily compatible with natural rubber when they are blended together. The compatibility of these polymers is enhanced by adding a suitable compatibilizer such as liquid natural rubber (LNR) in the blend. The LNR has been used as a compatibilizer to induce interaction between the rubber and plastic phases and thereby increases the homogeneity of the blend [2-4]. The radiation compatibilization of binary system has been a topic of interest for many years. The technique has been used efficiently and economically for the production of new or modified polymers [5].

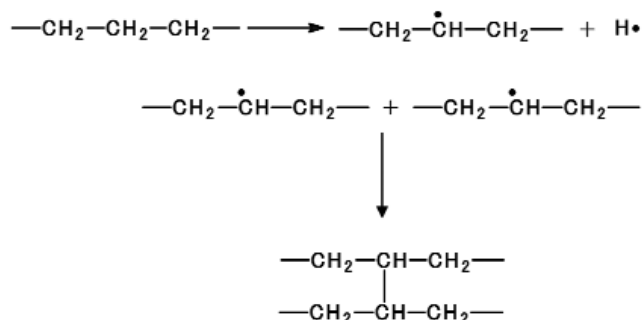
Radiation-initiated reactions can be classified as two types:

- (1) cross-linking and scission
- (2) grafting and curing

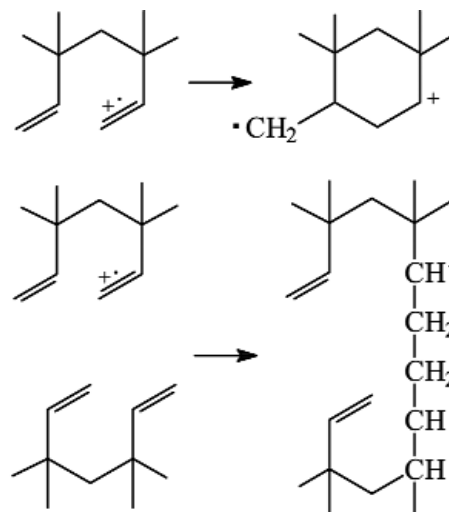
Cross-linking is the intermolecular bond formation of polymer chain. The degree of cross-linking is proportional to the radiation dose [6]. However, radiation cross-linking is only limited to few applications such as cross-linking of rubber for tyres, cable and pipe and heat-shrinkable tube.

Much work has been done on radiation cross-linking of uncross-linked polymers [6,7] and cross-linking of various rubbers and plastics by electron beam irradiation have been demonstrated [8,9]. The reaction involved is essentially achieved by a free-radical reaction [10,11]. However, to certain extent, it can take place also by an ionic reaction. The energy from the electron beam will knock out a hydrogen atom from the molecule and hence produce a reactive carbon radical (Scheme I and II).

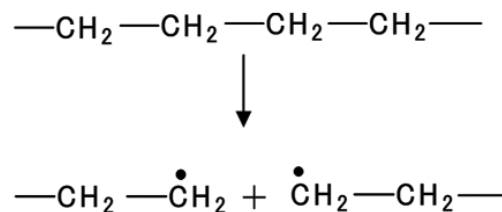
In contrast, scission is the opposite process of cross-linking in which the rupturing of C-C bond



Scheme I. Reactive carbon radical of polyethylene and cross-linking [12].



Scheme II. Reactive carbon radical of natural rubber and cross-linking [13].



Scheme III. Chain scission of polyethylene.

occurs [6] (Scheme III).

The addition of oxygen to polymeric free radicals form the peroxy species, which on decomposition form smaller molecules [6,12] (Scheme IV).

In this paper we have reported the result of irradiation of NR/LLDPE blends with electron beam at various radiation dosages in air at room temperature (25°C). The oxidation induced by radiation might be limited to the surface of samples. The changes in mechanical and physical properties and surface morphologies as a consequence of exposure to various radiation dosages are discussed.

EXPERIMENTAL

Materials

Natural rubber (SMR-L) was obtained from the Rubber Research Institute of Malaysia (RRIM), linear-low density polyethylene (LLDPE), Etilinas LL0220SA from

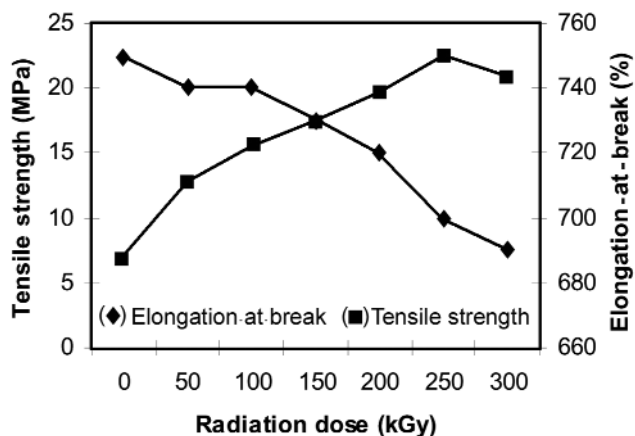


Figure 1. Tensile strength and elongation-at-break of NR/LLDPE blend.

with further increase of radiation dosage to 300 kGy. It is obvious that upon irradiation, enhancement in tensile strength occurs for NR/LLDPE blends [16]. This behaviour is believed to be due to the formation of radiation-induced cross-linking in the rubber and plastic phases as evidenced from the gel content value showed in Figure 2. Tensile strength maximizes at 22.4 MPa at a radiation dose of 250 kGy. The increase is triple as compared to the unirradiated samples. It indicates that the interactions between the components, which are due to radiation cross-linking, are the main factor influencing the properties of NR/LLDPE blends. Generally, the tensile strength increases with cross-links at lower cross-link density. However, at higher cross-link density the network becomes dense due to chain degradation and cross-links leading to inhomogeneity in the phase distribution.

Figure 1 shows the relationship between elongation-at-break of the sample and radiation doses. Generally increasing radiation dose results in reduction of elongation-at-break of the blend. Therefore, the reduction in elongation-at-break could be attributed to the reduced segmental mobility of polymer chains, which result from chain degradation and cross-linking of the polymers. In other words, the onset of chain degradation and cross-linking reduces the ability of the polymer chain to deform plastically hence a progressive reduction in elongation-at-break with increasing dose is noted [17]. As the radiation dose increases, more cross-links are produced in the sample matrix, which prevent the structural reorganization during drawing [18]. This ever increasing three-dimensional gel-like structure

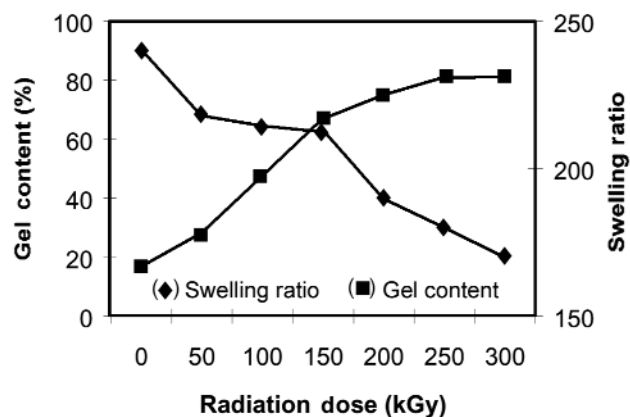


Figure 2. Gel content and swelling ratio of NR/LLDPE blend.

brings about a decrease in internal chain mobility and hence elongation.

The extent of radiation-induced cross-linking of polymers was estimated from the gel fraction determination. As Figure 2 shows the gel content of the samples increases with radiation dosage. It is observed that the gel content increases rapidly by increasing the radiation dosage up to 200 kGy, further increase in radiation reduces the increment and it is expected to level off.

The formation of a three-dimensional network structure on radiation is the most probable cause of gel formation due to increase in cross-link density via increasing radiation dose. As NR and LLDPE are organic polymers which are categorized radiation cross-linkable materials then such formation of cross-links upon irradiation are to be expected in them. As a result there is an increase in gel content and tensile strength in both materials.

Figure 2 shows that the swelling ratio decreases with radiation dose. This is the reflection of the gel content curve. It is observed that the results are nearly in accordance with those of gel content, supporting the formation of network structure on irradiation. Unirradiated samples were found to be soluble in toluene with swelling ratio at about 240%. However upon irradiation the polymers undergo cross-linking, and results in the formation of network structure. The solubility of the samples would be reduced significantly to 180% at a radiation dose of 250 kGy.

Gel is also formed when a strong interaction occurs between rubber and plastic phases. Swelling ratio is also an indicator of cross-links formed in the samples. The increases in cross-link density will result in a smaller

swelling ratio. However, the electron beam irradiation causes cross-linking, chain scission, and modification of network. Hence the net result of swelling ratio or gel is a combination of these three competitive reactions [19].

SEM Micrographs of extracted samples are shown in Figures 3a-3d of NR/LLDPE at different irradiation dosages. The micrograph consists of white and dark spots [20] indicating a morphological structure of a honey-comb type. The dark spots indicate the empty holes left behind by the NR after dissolving in toluene and the white spots belong to the insoluble LLDPE and cross-linked NR physically or chemically attached to the LLDPE particles [14].

Figure 3a shows that the surface is quite rough and consists of cross-linking particle size.

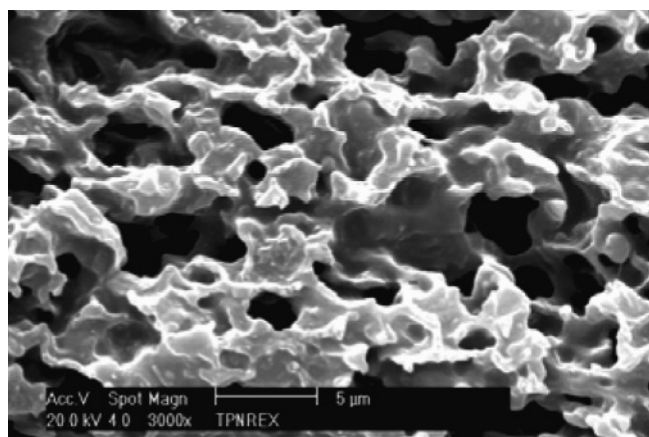
However, in Figures 3b-3d as the NR/LLDPE is exposed to longer duration doses, the morphology shows a slow reduction of dark spots and the white spots decrease and disappear, as well. The honey-comb struc-

ture in low dosage samples appears to transform gradually into a continuous matrix on increasing exposure to radiation.

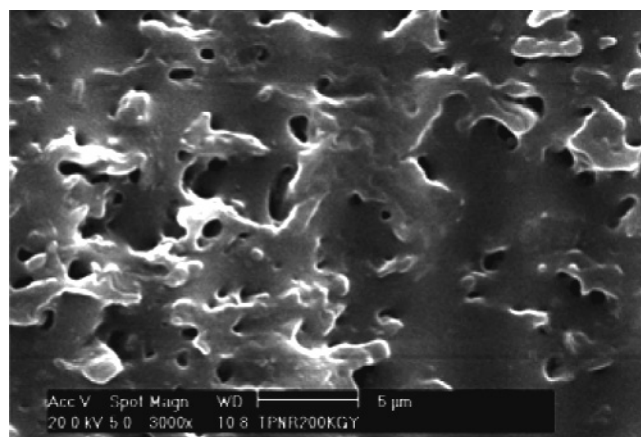
The smooth transformation of the morphology corresponds to the increase in cross-linking density in the rubber and plastic phases and rubber-plastic interaction. It is believed that electron beam irradiation induces cross-links in both phases. The interaction between the continuous (NR) and dispersed (LLDPE) components improves the blend compatibility and stability.

CONCLUSION

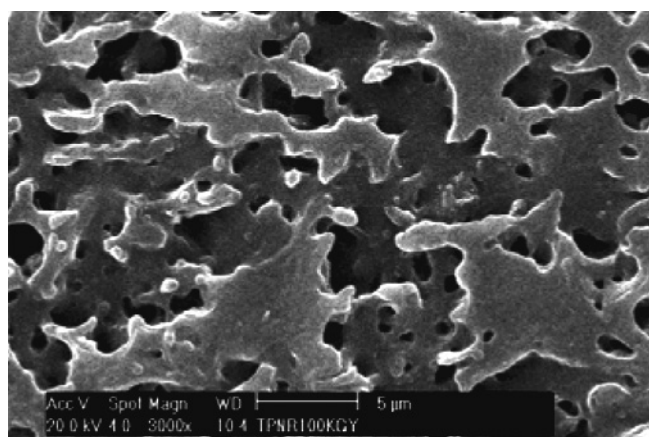
The electron beam radiation causes radical formation, chain degradation, and cross-linking between similar component (NR and PE) and different chains (NR-PE) in polymers. The extent of these reactions with the help of radiation dosage, makes the blend more stable and



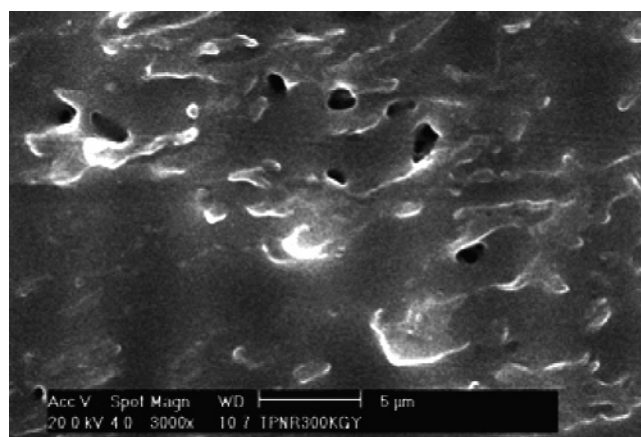
(a)



(c)



(b)



(d)

Figure 3. Extracted fracture surface of NR/LLDPE samples at different dose: (a) NR/LNR/LLDPE, (b) NR/LNR/LLDPE/ 100 kGy, (c) NR/LNR/LLDPE/ 200 kGy, and (d) NR/LNR/LLDPE/ 300 kGy.

homogeneous. In such case, the physical and mechanical properties would change accordingly.

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