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Electron Beam Cross-linking of Carbon Black Filled NR/LLDPE Blends

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ABSTRACT

Blends of NR/LLDPE were prepared by melt blending in a Haake Rheomix at 140°C with a rotor speed of 50 rpm and 15 min mixing. Liquid natural rubber (LNR) and carbon black were incorporated into the blend as a compatibilizer and filler, respectively. The effect of electron beam irradiation on the properties of carbon black filled NR/LLDPE blends has been studied over a range of radiation doses and loadings. Compared to unfilled irradiated NR/LLDPE blends, tensile strength and modulus at 100% increase with increase in the amount of the carbon black filler. Similar improvements in these properties are observed with an increase in both the radiation dose and the amount of the filler up to a certain level. The results are explained with the help of insoluble gel content and swelling index analysis. It is observed that higher reinforcement in the case of the filled samples is obtained by electron beam irradiation modification, as compared to that of using the conventional curing system.

Key Words:
electron beam;
filler; radiation;
carbon black;
blends;
cross-linking.

INTRODUCTION

Thermoplastic properties can be incorporated into natural rubber (NR) via blending with any compatible thermoplastic such as polyethylene (PE) or polypropylene (PP). Such blends are generally termed thermoplastic natural rubber (TPNR) and the material, by the physical properties exhibited, is categorized as an elastomer lying between rubber and plastic [1]. Carbon black was incorporated as reinforcement filler in the NR/LLDPE blends. Carbon black has unique ability to enhance

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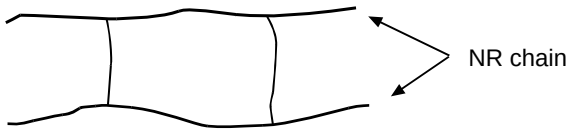
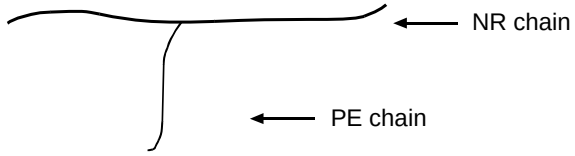
the physical properties of elastomers [2]. This well-documented phenomenon [3,4] termed as reinforcement , has a profound effect on today s tyre and rubber industry. Carbon black is used in plastics to alter key physical properties of the compound, which determines their applications in a given market segment [5]. The effects of variation of filler loading on mechanical properties of polymer blend are reported in the literature [6,7]. Electron beam modification on filled rubber/plastic has been studied earlier [6,8]. It is well known that natural rubber (NR) and polyethylene (PE) belong to the class of cross-linkable polymers while natural rubber is more prominent in cross-link due to the presence of unsaturated polyisoprene chain [9,10,11]. The typical reactions between the radicals formed are proposed as follows:

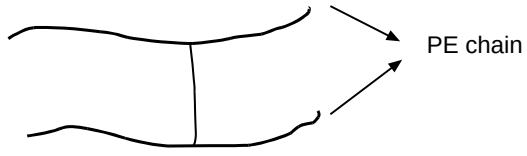
(a) Cross-linking between polyisoprene chain of natural rubber



(b) Grafting of polyethylene on the polyisoprene chain of natural rubber



(c) Cross-linking between ethylene chain of polyethylene



However, there is no study on the electron beam modification of NR/LLDPE blend in the presence of carbon black. This study was basically to investigate the effects of various carbon black loadings and radiation dose on the mechanical properties of natural rubber and linear low-density polyethylene (LLDPE) blends.

EXPERIMENTAL

Materials

Natural rubber (SMR-L) was supplied by the Malaysian Rubber Board (MRB) and linear low-density polyethylene (LLDPE), Etilinas LL0220SA was obtained from polyethylene Malaysia Sdn. Bhd. Carbon Black (N110) was bought from Cabot Corporation. Liquid natural rubber (LNR) was prepared in our laboratory by a photochemical technique [12].

Formulation

The 60/40 NR/LLDPE blend was prepared by mixing 45% by weight of NR, 15% by weight of LNR with 40% by weight of LLDPE. Carbon black was added by volume percent. The total weight amounted to 44.45 g.

Blend Preparations

Blends of NR/LLDPE were prepared by melt blending in a Haake Rheomix at 140 C, with a rotor speed of 50 rpm and 15 min mixing. NR was charged into the mixing chamber and mixed for 1 min. LNR was then added, and the blending was continued for 3 min. Then, LLDPE was charged, and the mixing was continued for 2 min. Finally carbon black was added, and blending was continued for another 9 min. The blends were taken out and were compression moulded into 1 mm thick sheets under a pressure of 150 kg/cm^2 in an electrically heated hydraulic press at 140 C for 3 min. The sheets were immediately cooled between two plates of a cold press at 25 C. The sheets were then irradiated with electron beam (using 3 MeV electron-beam machine, manufactured by NHV, Japan) for various doses.

Physical Testing

Physical tests for the tensile strength, elongation-at-break and modulus at 100% were determined on dumbbell shaped samples using a Toyoseiki model Strograph-RI with a load cell of 1 kN at room temperature in accordance with the standard rubber procedure of ASTM D412 and standard plastic procedure of ASTM D638. The cross-head speed of 250 mm/min was used to justify serving the rubber/plastic composition. The sample dimensions were according to BS 6746 standard. The tests were carried out on seven sample pieces for each blend, and the readings were calculated from the best five samples.

Insoluble Gel Content and Swelling Index

Insoluble gel contents were determined by the Soxhlet extraction technique using toluene as solvent. The samples were extracted for 24 h and air dried before keeping in vacuum oven at 60 C until constant weight. The gel content was calculated as follows:

Insoluble gel content (%) =
(wt after extraction / wt before extraction) × 100%

For swelling test, ASTM D 3616 was followed. Weighed samples were immersed in toluene for 24 h at room temperature. The surface of the swelled samples were then immediately blotted with filter paper and weighed. The swelling ratio was defined as:

$$\text{Swelling index} = \frac{W_S}{W_I}$$

W_S and W_I were the weights of swelled and dried samples, respectively.

RESULTS AND DISCUSSION

Effect of Filler Loading

Tensile strength of a polymer is a function of cross-link density and energy dissipation [13]. Table 1 shows the variation of mechanical properties (tensile strength, modulus at 100% and elongation-at-break), insoluble gel content and swelling index of filled NR/LLDPE blends with different loadings of carbon black. Tensile strength (Figure 1) of the samples increased with increased filler loading.

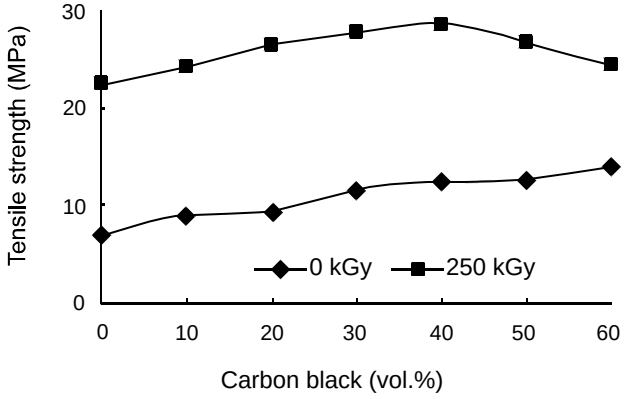


Figure 1. Effects of carbon black loading on tensile strength of NR/LLDPE blends.

Table 1. Effects of carbon black loading on the properties of filled NR/LLDPE blends.

Carbon black (Vol %)	Tensile (MPa)	Modulus (MPa)	Elongation-at-break (%)	Swelling index	Gel content (%)
0	6.8	2.7	750	3.75	16.5
10	8.8	2.8	720	3.29	24.4
20	9.2	2.9	700	3.26	27.4
30	11.4	3.5	650	3.15	35.6
40	12.3	3.7	600	2.92	43.8
50	12.5	4.4	580	2.70	45.2
60	13.8	6.3	550	2.19	55.6

It is indicated that the degree of reinforcement of NR/LLDPE blends increased upon the extent of polymer-filler interaction [14]. Generally, polymer-filler interaction is lower, especially at lower concentration of filler.

The elongation-at-break (Figure 2) decreased with increased in filler loading. This reduction is due to stiffening of the matrix by the black particles or filler. In fact, with a further increased in filler loading the molecular mobility decreased due to the formation of physical bonding between the filler particles and polymer chain that stiffen the matrix [14]. The increase in modulus (Figure 3) with carbon black loading indicates the ability of carbon black to impart greater stiffness to NR/LLDPE blends [15]. All these observations can be explained on the basis of apparent increase in the degree of cross-linking as measured by insoluble gel content (Figure 4) and swelling index (Figure 5).

Insoluble gel content increased with increasing percentage of carbon black loading. However, swelling index decreased with increasing amounts of carbon

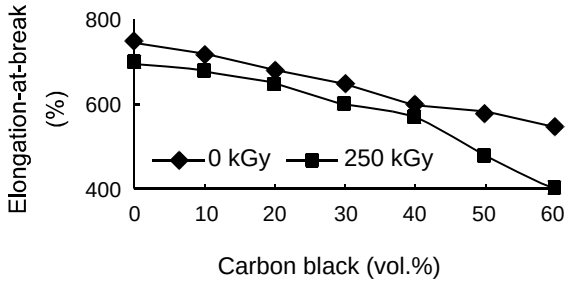


Figure 2. Effects of carbon black loading on elongation-at-break of NR/LLDPE blends.

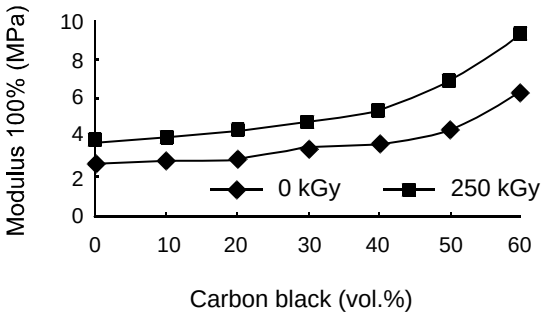


Figure 3. Effects of carbon black loading on modulus of NR/LLDPE blends.

black loaded in the blends. The increase of insoluble gel content and decrease in swelling index with carbon black loading are due to the formation of a network structure, bound polymer layer and increment of polymer-filler interaction [16]. It is also suggested that carbon black influences the thermally induced interaction between natural rubber and LLDPE phases [6].

Table 2 indicates the effects of filler loading on the properties of carbon black filled NR/LLDPE blends at constant radiation dose, 250 kGy. Tensile strength (Figure 1) increased with increasing in filler loading up to 40% and then decreased. Elongation-at-break (Figure 2) decreased with increasing in filler loading. Tensile strength increased as a result of the additional reinforcement of the polymer phases due to cross-linking electron beam irradiation [6].

The tensile strength increased with cross-linking at lower cross-link density. However, at higher cross-link density the network was so dense that there was little energy dissipation in the matrix and the energy supplied was utilized for breaking the bonds [17]. The reduction of tensile strength was also due to less wetting of the black particles by rubber chains [7]. Generally, electron beam irradiation induced cross-linking in rubber-plastic phases and enhanced the polymer-filler interaction. It is suggested that radiation plays the important role in order to enhance mechanical properties of the blends. The increase in modulus at 100% (Figure 3) and reduction of elongation-at-break with carbon black loading were proportional to the number of cross-link formed [18]. This was also due to stiffening of the matrix by filler.

Table 2. Effects of carbon black loading on the properties of filled NR/LLDPE blends at constant radiation dose (250 kGy).

Carbon black (Vol %)	Tensile (MPa)	Modulus (MPa)	Elongation-at-break (%)	Swelling index	Gel content (%)
0	22.4	3.8	700	2.88	91.3
10	24.1	4.0	680	2.66	91.5
20	26.3	4.4	650	2.51	91.7
30	27.6	4.8	600	2.29	91.9
40	28.5	5.4	500	2.12	92.1
50	26.6	6.9	480	2.06	92.2
60	24.3	9.3	400	1.85	93.8

All these observations also can be explained on the basis of apparent increased in the degree of cross-linking as measured by insoluble gel content (Figure 4) and swelling index (Figure 5).

In conclusion, from Table 1 and Table 2, both factors such as electron beam irradiation and filler influenced the mechanical properties of NR/LLDPE blends significantly.

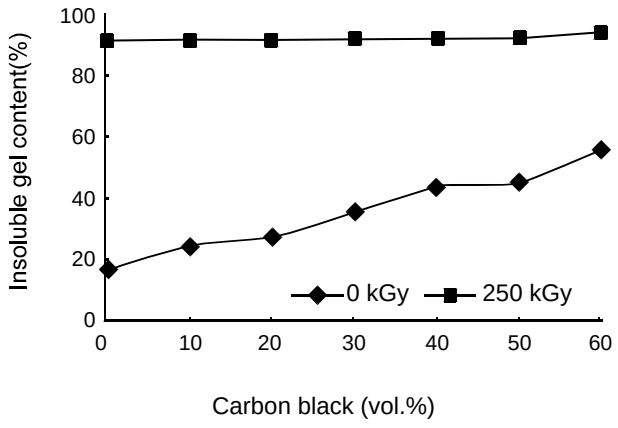


Figure 4. Effects of carbon black loading on insoluble gel content of NR/LLDPE blends.

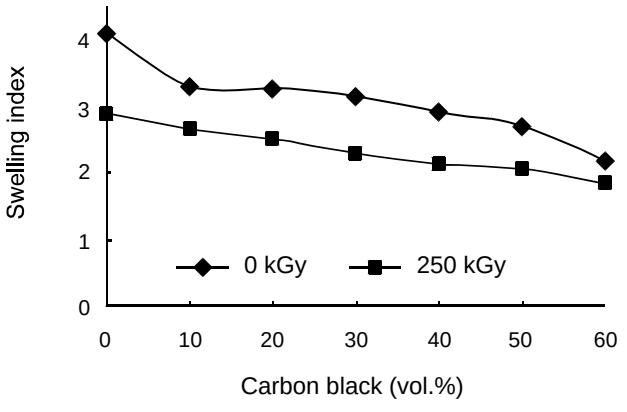


Figure 5. Effects of carbon black loading on swelling index of NR/LLDPE blends.

Table 3. Effects of radiation dose on the properties of NR/LLDPE blends.

Rad. dose (kGy)	Tensile (MPa)	Modulus (MPa)	Elongation-at-break (%)	Swelling index	Gel content (%)
0	6.8	2.7	750	3.75	16.5
50	12.8	2.9	740	3.30	27.2
100	15.6	3.1	740	3.28	45.9
150	17.5	3.3	730	3.26	66.3
200	19.6	3.5	720	2.99	74.9
250	22.4	3.8	700	2.88	80.6
300	20.9	4.5	690	2.78	81.0

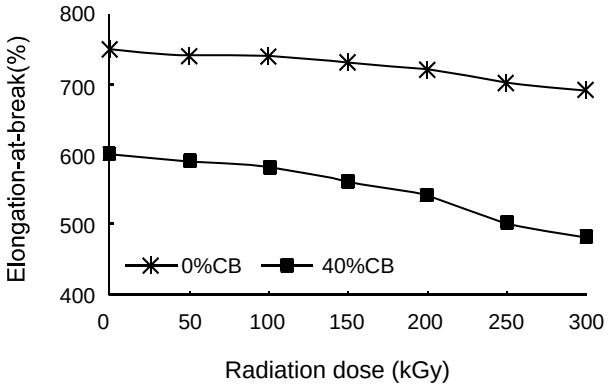


Figure 7. Effects of radiation dose on elongation-at-break of NR/LLDPE blends.

Effect of Radiation Dose (at a Fixed Loading of Carbon Black)

Table 3 illustrates the mechanical properties, insoluble gel content and swelling index as a function of irradiation dose. It is shown that upon irradiation the tensile strength (Figure 6) of NR/LLDPE blends increased rapidly up to 250 kGy and started to decrease with the further increase of radiation dose to 300 kGy. The increment of tensile strength was due to cross-linking in the polymer phases. The reduction of tensile strength is most likely to be caused by the chain scission at higher radiation dose. Table 3 also showed the relationship between elongation-at-break (Figure 7), modulus (Figure 8), and irradiation dose of the samples.

Generally increasing the radiation dose results in reduction in elongation-at-break of the blends. As dose increases more cross-links are produced in the sample matrix, which prevents the structural reorganization during drawing. This phenomenon will increase the three-dimensional gel-like structure resulting in a decrease in internal chain mobility and elongation [19]. The result will be supported and could be explained on the basis of insoluble gel content (Figure 9) and swelling ratio (Figure 10). Insoluble gel content of the samples was irradiated at different radiation doses. It is observed that gel content increased rapidly up to 250 kGy and increased gradually with further increase in radiation dose. The increase in the gel content (Figure 9) with radiation dose is due to the formation of a three-dimensional network structure. Swelling ratio (Figure 10) decreased with irradiation dose. It is observed that the results are nearly in line with those of gel content, supporting the formation of network structure on irradiation. From the present data it seems probable that with an increase of the radiation dose, the number of

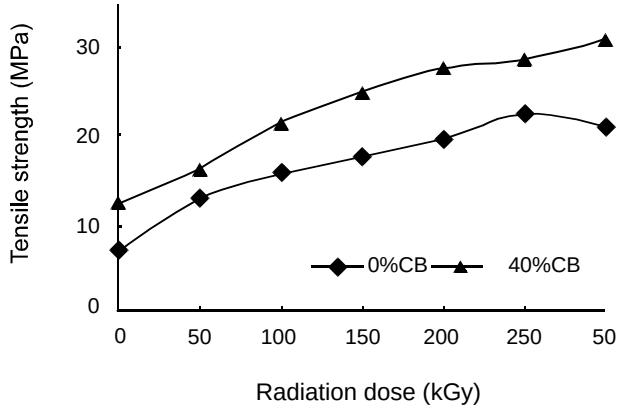


Figure 6. Effects of radiation dose on tensile strength of NR/LLDPE blends.

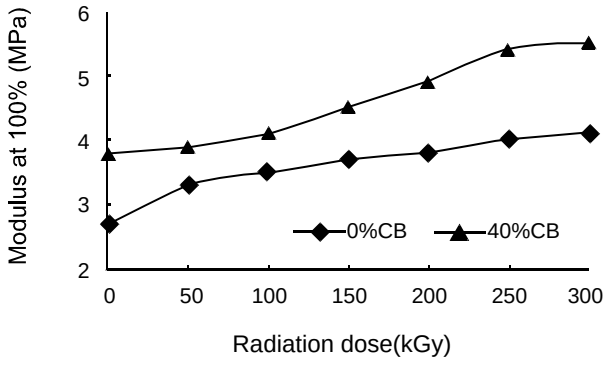


Figure 8. Effects of radiation dose on modulus at 100% of NR/LLDPE blends.

Table 4. Effects of radiation dose on the properties of carbon black filled NR/LLDPE blends (at a fixed level of carbon black, 40 vol%).

Rad. dose (kGy)	Tensile (MPa)	Modulus (MPa)	Elongation-at-break (%)	Swelling index	Gel content (%)
0	12.3	3.7	600	2.92	43.8
50	16.1	3.9	590	2.78	57.2
100	21.2	4.1	580	2.53	68.8
150	24.8	4.5	560	2.33	78.2
200	27.6	4.9	540	2.25	85.5
250	28.5	5.4	500	2.12	92.1
300	30.9	5.5	480	2.00	93.0

macroradicals produced is higher; so there is a higher probability for collision between macroradicals, because of which the radical-radical recombination as well as the radical addition across π-electrons to generate cross-linkings is more favoured [17]. Cases involving oxidative cross-linking (irradiation being carried in air) and chain scission can also prevail. Chain scissions are supposed to complete with cross-linking at higher doses. The increase in the extent of cross-linking can be accounted that chain scission leads to entanglement coupling which then act as cross-links [18].

Table 4 shows the variation of mechanical properties, insoluble gel content and swelling index of carbon black filled NR/LLDPE blends mixed with a constant loading of carbon black and irradiated with various irradiation doses. Compared to irradiated samples, tensile strength (Figure 6) and modulus at 100% (Figure 8)

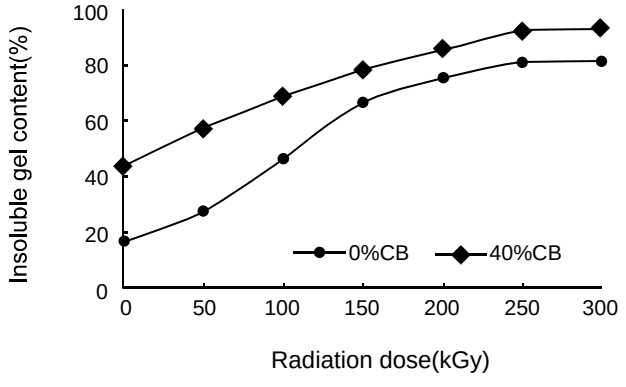


Figure 9. Effects of radiation dose on insoluble gel content of NR/LLDPE blends..

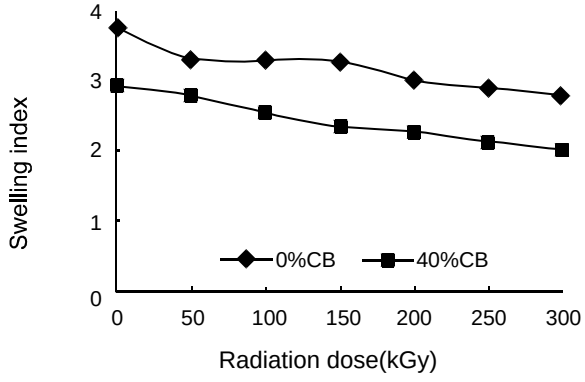


Figure 10. Effects of radiation dose on swelling index of NR/LLDPE blends.

of irradiated samples are increased with increasing radiation doses. However, elongation-at-break (Figure 7) decreased with increasing radiation doses. The reduction of elongation-at-break is due to stiffening of the matrix by electron beam. It is apparent that filler-polymer bonding increases the value of cross-link density. The result further indicates that at a higher radiation dose there is an additional bonding between the filler and polymer through the large number of free radicals on the carbon black and polymer. Increased radical yields on the black-polymer interphase with an increase in the concentration of the curing agent (radiation dose) have been reported in the literature [6]. Therefore, an increased radical recombination is likely to generate strong chemical linkage with an increase in the radiation dose. The increase in modulus (Figure 8) with radiation dose of the blend indicates the ability of electron beam irradiation to impart greater stiffness to NR/LLDPE blend. All these observations can be also explained on the basis of apparent increase in resistance to flow and increase in the degree of cross-linking as measured by gel content (Figure 9) and swelling index (Figure 10).

CONCLUSION

Significant changes in mechanical properties of the blends are due to the reinforcement of carbon black filler and strong interaction between carbon black and polymer matrix upon irradiation. Higher filler loadings and radiation doses lead to higher cross-link densities

and better mechanical properties.

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