Reinforced Material from Reclaimed Rubber/Natural Rubber, Using Electron Beam and Thermal Treatment

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ABSTRACT: Reclaimed rubber powder (RRP) was treated by the addition of maleic anhydride (MA) to impart desired properties suitable for self-adhesive sheets and concrete lining applications. The produced MA-RRP was mixed with natural rubber (NR) with various compositions. A fixed 1 : 1 blend ratio of NR : RRP was reinforced with various contents of glass fiber (GF) in an open two-roll mixing mill. The composites were irradiated using a 1.5 MeV electron beam accelerator at 30 and 50 kGy irradiation doses. Different properties of composite such as tensile strength, elongation at break, hardness, swelling behavior in different media, thermal stability, and scanning electron microscope (SEM) for both unirradiated and irradiated samples with respect to the RRP and GF content were investigated. Results show that the tensile strength and swelling resistance increase with increasing RRP content in the NR/RRP blends, whereas the elongation at break exhibit opposite trend. It can be observed that the hardness increases with increasing the fiber content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2569–2578, 2007

Key words: reclaimed rubber powder; natural rubber; glass fiber; electron beam; self-adhesive sheets; concrete lining applications

INTRODUCTION

Increasing environmental concerns and legislation have resulted in significant pressure to reduce, reuse, or recycle various waste rubber products. Scrap rubbers are made up of rubber that does not meet processing and product specifications, leftover rubber from manufacturing activities, and also of old and defective rubber products. The scrap rubbers are waste and usually discharged. The discarded scrap rubber does not degrade rapidly enough and this causes environmental pollution. To reduce this pollution, there is a need to recycle scrap rubber. Waste rubber powder is one of the materials that may be converted into several useful products.[1–5] Acetta and Vergnaud[6,7] tried to upgrade scrap rubber powder by vulcanization without new rubber. Mathew et al.[8] reported the recycling of natural rubber (NR) latex waste and its interaction in epoxidized NR.

The reutilization of ground rubber powder as a dispersed electrometric phase in a thermoplastic matrix offers an opportunity to design second generation materials, which would be recyclable due to the thermoplastic matrix and which potentially could present thermoplastic elastomer (TPE)-like mechanical behavior.[9] Indeed, a particular family of TPE, called thermoplastic vulcanizates (TPVs), is obtained by dispersing an uncrosslinked rubber phase into a thermoplastic matrix by melt-blending, and dynamically crosslinking that rubber phase in the melt.[10] Recycling end-of-life GTR powder as a functional filler in a thermoplastic matrix with the aim of obtaining materials of similar morphology and behavior is particularly interesting, since it turns into an advantage the three dimensional network nature of rubber, is generally a problem for recycling (compared to thermoplastics) due to the insolubility and nonmelting-associated properties.

Baker and coworkers[11–13] reported that the use of several compatibilizers of ground rubber tires to improve the adhesion between ground rubber tires and thermoplastic matrices. One drawback of such blends is a comparatively weaker matrix. One way to overcome this problem is by using short fibers as reinforcing fillers. This will be an efficient route to use scrap fibers accumulated from fiber industries. Short-fiber-reinforced rubbers have become very important due mainly to their processing advantages and technical properties. The composites are of great interest in many industrial applications, notably the production of hose, oil seal, and complex-shaped mechanical parts. The mechanical properties of the composites such as modulus, tensile strength at break, and ultimate elongation depend on fiber orientation, aspect ratio, interfacial adhesion, and fiber loading.[14–19] The effect of the adhesion system on the thermal stability of NR–polyester short-fiber composites has been examined.[20] Different short fibers (glass, carbon, cellulose, polyamide, and polyester) have been added to

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the styrene–butadiene–rubber (SBR) matrix, filled with inorganic semireinforcing mineral filler. The composite-cured properties have showed a remarkable anisotropy.

Ionizing radiation offers unique possibilities for application to the problem of recycling polymer,[21] due to its ability to cause crosslinking or scission of a wide range of materials without dissolving the sample or having some chemical initiator incorporated in the matrix.

Radiation-cross-linking of fiber–matrix composites using an electron beam is a promising application, which has been developed in recent years.

In the present work, we report the results of our investigations on mechanical and thermal properties, and swelling behaviors of reclaimed rubber powder (RRP)-filled NR compounds. A morphological study of the tensile fracture surfaces of the NR compounds was also carried out. The incorporation of SGF into NR/reclaimed rubber blend plays an important role for increasing its thermal stability.

EXPERIMENTAL

Materials

Natural rubber latex (NRL) was obtained from TOPTEX, Malaysia. The latex is 60% concentrated and high ammonia-stabilized. Reclaimed rubber powder (RRP) of particle size 80 mesh was kindly provided by Narobine, Egypt.

Maleic anhydride (MA) was obtained from Merck (Munich, Germany); other compounding rubber ingredients were of commercial grade used in industry.

The fluids used for weight swelling test were ESSO Extra multigrade motor oil 20 W-50 B/SF/CC (Exxon, Houston, TX) and Lockheed super 105 hydraulic fluids, a product of Leamington Spa, UK.

Sheet preparation

RRP was washed several times with petroleum ether and then with boiling water, and dried at 50°C in vacuum oven. The mixing of RRP with maleated NR and glass fiber (GF) in different ratios was achieved using open mill at a temperature of about 70°C (Tables I and II). The sheeted out stock was compression-molded in an electrically heated hydraulic press at 150°C for 7 min to ensure the homogeneity of the blends.

TABLE I
Uncured Natural Rubber Latex/Reclaimed Rubber Powder (NRL/RRP) Blend Compositions

Rubber (phr)	S1	S2	S3	S4	S5	S6	S7
NR	100	85	70	60	50	40	30
WR	0	15	30	40	50	60	70
MA	0	5	5	5	5	5	5

TABLE II
Uncured Natural Rubber/Reclaimed Rubber Powder/ Glass Fiber (NR/RRP/GF) Blend Compositions

Rubber (phr)	S8	S9	S10	S11	S12	S13
NR	50	50	50	50	50	50
WR	50	50	50	50	50	50
MA	5	5	5	5	5	5
GF	0	10	20	30	40	50

Electron beam radiation source

A 1.5 MeV electron accelerator at 30 and 50 kGy irradiation doses was used. It is installed at the National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt.

Mechanical measurements

Tensile properties of the films were measured by using HOUNS FILD testing machine, England, connected to a personal computer. The ISO 37-1977 (E) and ISO 34-1975 (E) standards were followed to measure tensile strength and elongation at break, respectively.

Swelling tests

Swelling index was measured using the following method. Three pieces of sample of approximately uniform size and weight ($\sim$ 0.5 g) were accurately weighed (W_1) and immersed in 50 mL of toluene at room temperature for 24 h. After that the sample was taken out and put between two pieces of filter paper, then put between two sheets of glass (each weighted 98.4 g), kept for 5 s and transferred to weighing bottle and reweighed (W_2). The swollen gel were then dried in a vacuum oven at 60°C for 15 h and reweighed again (W_3); the swelling index (I) was calculated as below

$$I = W_3/W_2$$

Swelling of rubber composites in toluene was carried out at room temperature (25°C) for 24 h, according to ASTM D471-97. Swelling tests in motor oil and brake fluid were conducted at room temperature for 7 days.

Scanning electron microscope

An ISM-5400 scanning electron microscope (JEOL, Tokyo, Japan) was used for morphological observation of freeze-fractured samples after vacuum-coating with gold.

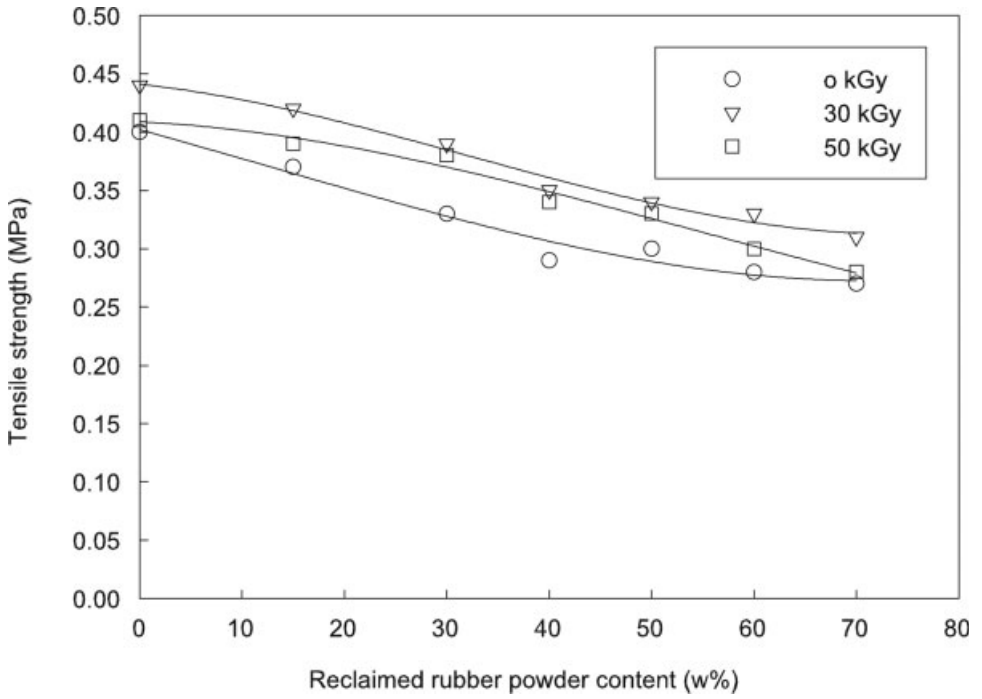

Figure 1 Variation of the tensile strength at break of different ratios of NR/RRP with various irradiation doses.

Thermogravimetric analysis

A Type TGA-50 system (Shimadzu, Kyoto, Japan) in nitrogen atmosphere at 20 mL/min was used in this study in the temperature range from ambient to 600°C at heating rate of 10°C/min.

RESULTS AND DISCUSSION

Mechanical properties

The variation of tensile strength at break (T_b) with the addition of reclaimed rubber is shown in Figure 1. The lowering of tensile strength with the addition of RRP is due to the lower molecular weight of the reclaimed rubber. The high shear and temperature during the reclamation process severely breaks down the molecular chains to shorter segments. Incorporating more of this low-molecular-weight fraction results in progressive reduction in the tensile strength.

The high-energy irradiation of polymers creates free radicals by the scission of the weakest bonds. These new entities react with each other or with molecular oxygen if the exposure environment contains it. The effect of EB irradiation on T_b of NR/RRP/5% MA with various compositions at different irradiation doses is shown in the same figure; the T_b of the samples increased with the corresponding increase in irradiation dose on 30 kGy and after that a decrease was observed. Low T_b values at 50 kGy indicate the high level of degradation (the scission of crosslinks or scission of a fraction of rubber chain at points between crosslinks can occur) in the mixture containing reclaimed rubber. This observation has been also discussed by Charlesby.[22] According to him, in crosslinkable polymers such as rubbers, a maximum tensile strength is achieved by obtaining a certain crosslinking density. However, subsequent decreases in strength as further crosslinks are introduced may be due to the interference of these crosslinks with crystallization.

Figure 2 shows the variation of elongation percent at break (E_b) with RRP loading. E_b decreases with increasing RRP loading; there is a gradual reduction from 313 to 202% at 0 to 80 parts RRP loading, respectively. The low molecular weight and the presence of reinforcing filler in the RRP may inhibit molecular orientations, causing the sample to fail at lower elongation. Also, this observation is due to the presence of crosslinking rubber particles and other ingredients in RRP, which limit the flow and mobility of the NR/RRP blends particularly at a higher content of RRP. There is a uniform drop in the elongation at break values of the composites after irradiation, as shown in Figure 2. These results indicate that the decrease in the E_b with increasing irradiation dose is due to effective increase in crosslinking at higher irradiation doses, which renders them unable to stretch upon deformation.

The variation of T_b with fiber content of NR/RRP/MA (50/50/5) composites is given in Figure 3. The tensile strength gradually increases with increasing GF content for nonirradiated composites, which hinders the fracture front and makes stress more evenly distributed. The similar trend was found for irradi-

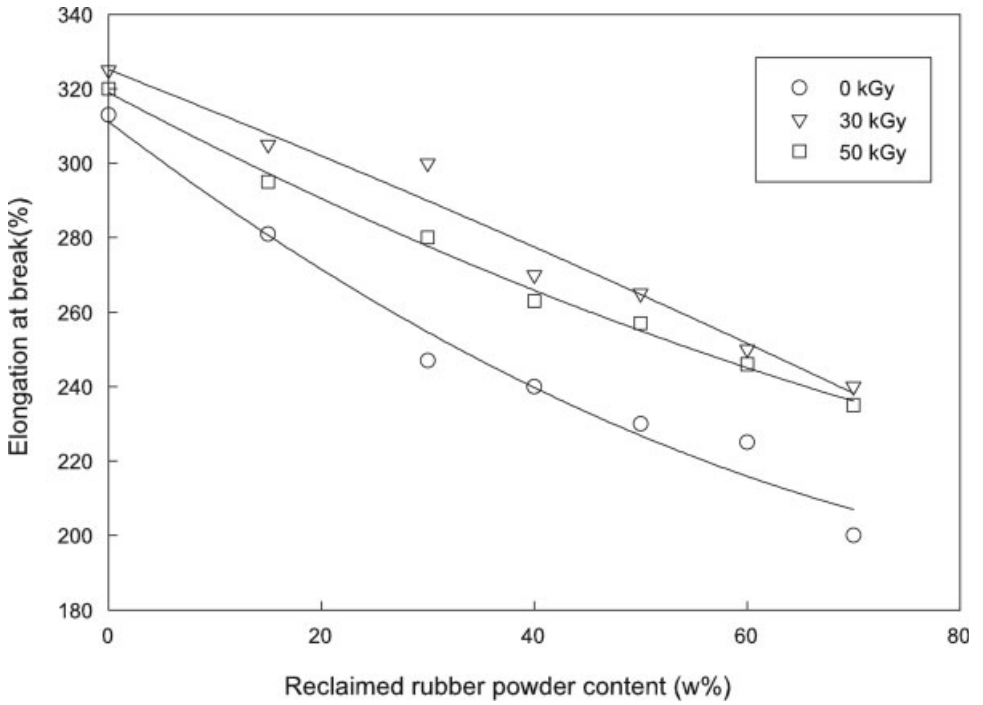

Figure 2 Variation of the elongation at break of different ratios of NR/RRP with various irradiation doses.

ated composites, where the tensile strengths increased by increasing the irradiation doses. These results were attributed to the formation of crosslinking between the molecules participated in the rubber chains by e-beam effects. Scientists confirmed such explanation; by the fact that the bombardment of electrons makes rubber molecules become excited and then in ionized states.[23] Such free radicals were responsible for cross-link reactions between the chains of the rubber matrix.

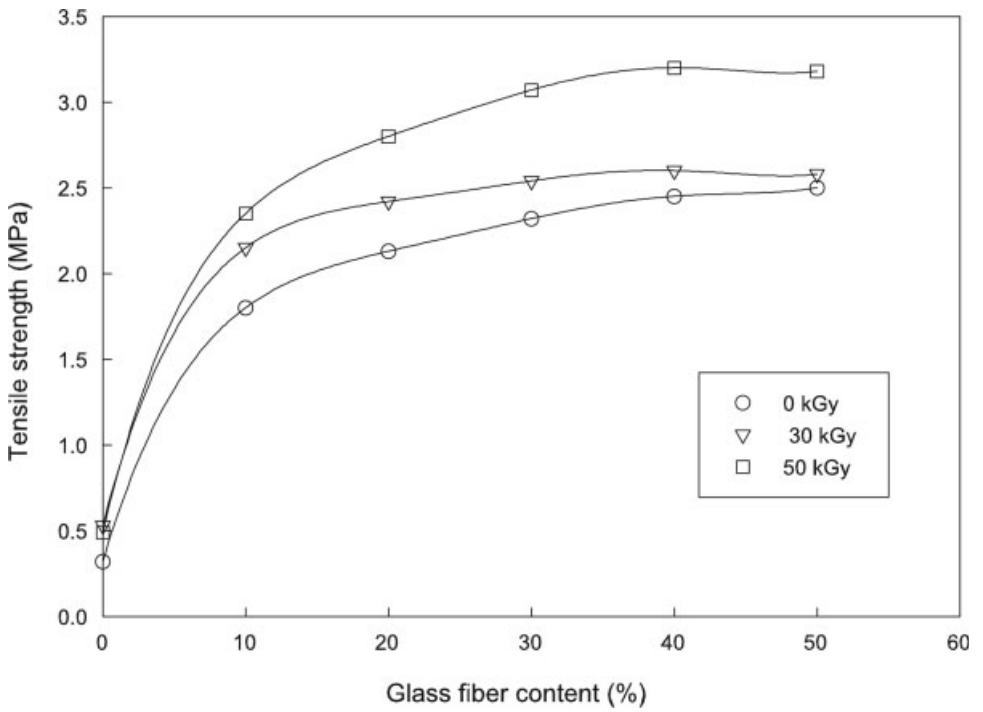

Figure 3 Variation of the tensile strength at break of NR/RRP (50/50) with different glass fiber loading at different irradiation doses.

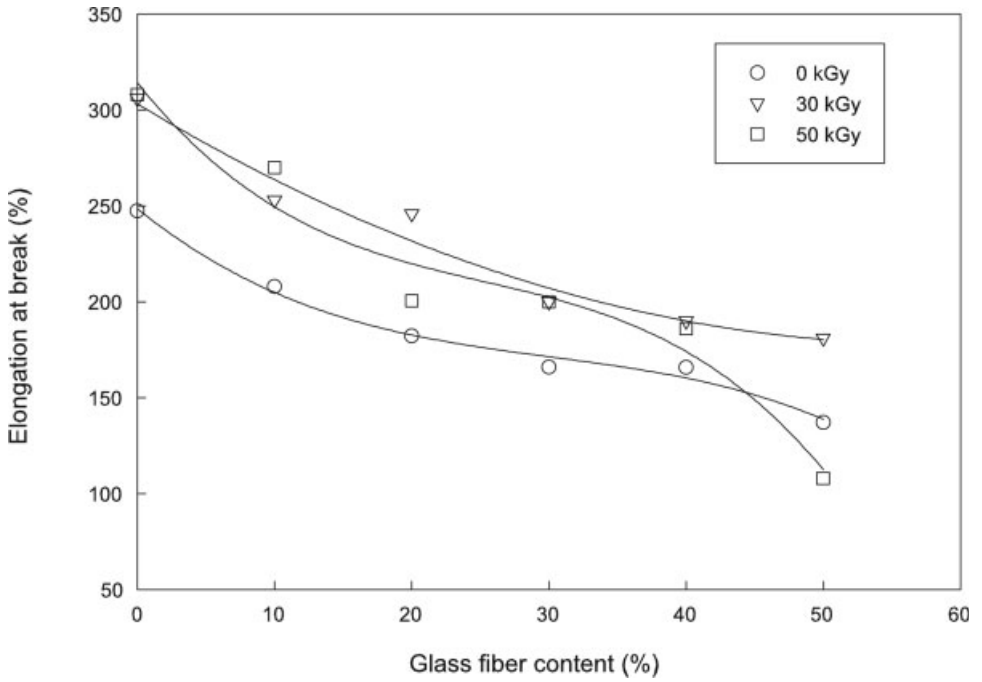

Figure 4 Variation of the elongation at break of NR/RRP (50/50) with different glass fiber loading at different irradiation doses.

Figure 4 shows the E_b for both nonirradiated and irradiated reinforced films. It is revealed that elongations of nonirradiated reinforced films are lower than those of the corresponding irradiated ones. The elongation at break decreases with increasing fiber, which inhibits the orientation of molecular chains and hence decreases the elongation percent.

Hardness

Figure 5 shows the effect of GF content on hardness for NR/WR/MA (50/50/5)% composites. It can be observed that the hardness increases with increasing the fiber content as mentioned before in tensile strength.

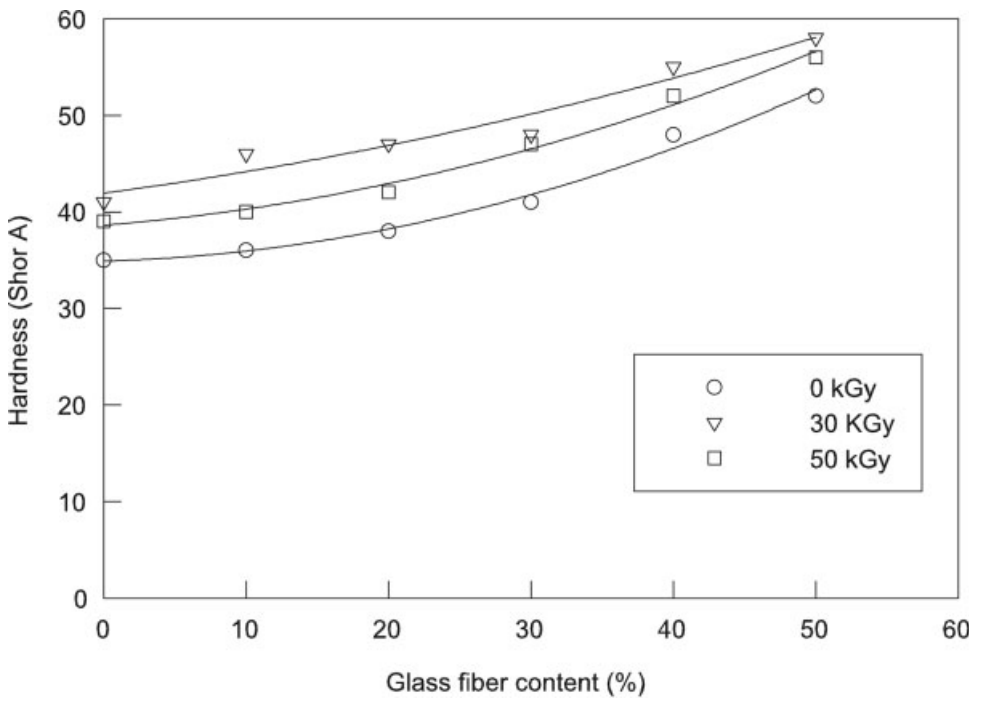

Figure 5 Effect of glass fiber content on the hardness (shor A) of NR/RRP (50/50) at different irradiation dose.

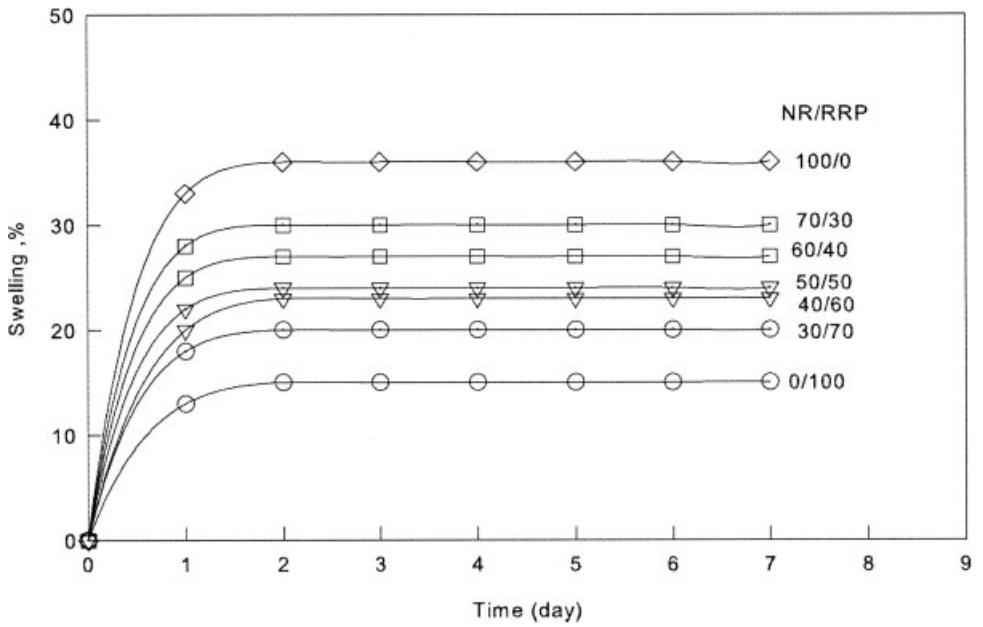

Figure 6 Swelling–time relationship of partial replacement of NR with RRP for NR/RRP/MA blends in motor oil.

The e-beam irradiation of a polymer is known to affect its hardness. The incident ion undergoes loss of energy upon its passage through the polymer by two mechanisms, namely, electronic stopping and nuclear stopping. The nuclear stopping involves the energy loss by displacing atoms in the medium as a result of nuclear collision, which is most effective when the incident ions are heavy. The nuclear collision causes the release of pendant atoms in the polymer resulting in bond breakage. This phenomenon is known as chain scission.[24] The other important mechanism is the electronic stopping in which the stripped ion reacquires its orbital electrons as it also creates a large number of secondary electrons; the electron stopping also causes loss of energy. The electronic stopping causes more crosslinking than scission that occurs whereby two free bonds dangle on neighboring chains units.[25] In the present study, the ions used are

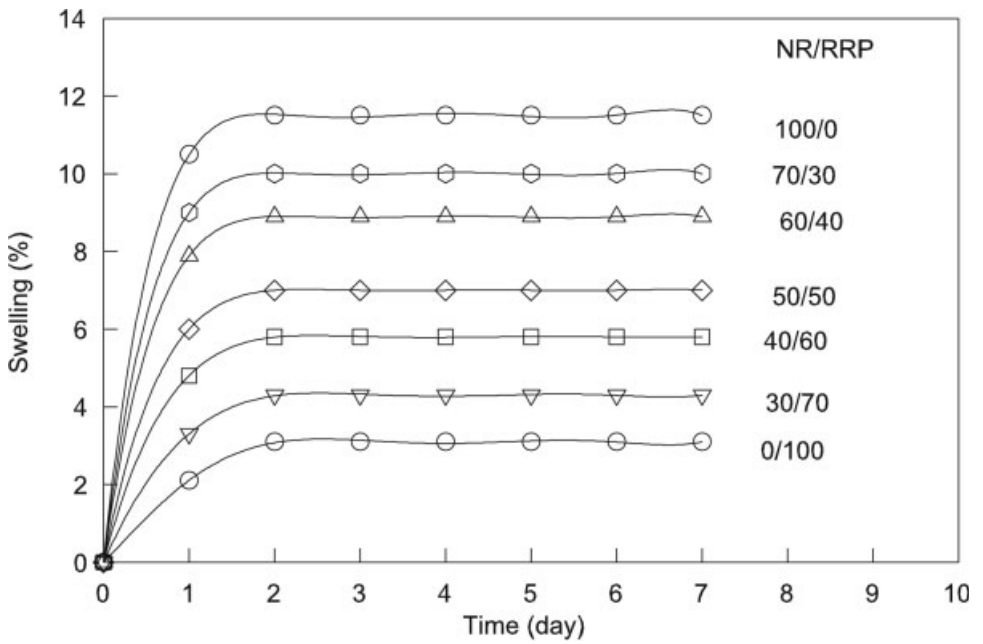

Figure 7 Swelling–time relationship of partial replacement of NR with RRP for NR/RRP/MA blends in fluid oil.

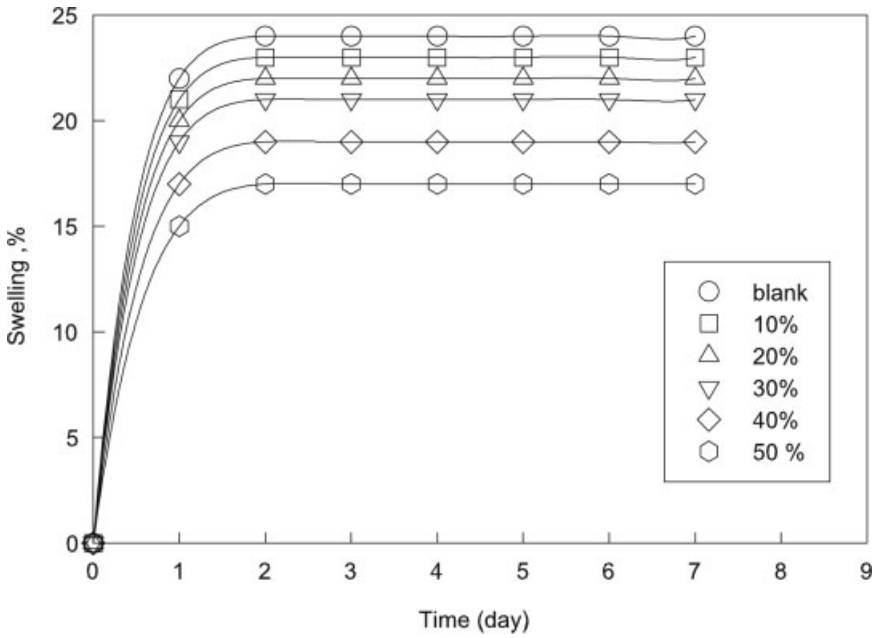

Figure 8 Swelling–time relationship of NR/RRP/MA (50/50/5) (wt %) with different ratios of glass fiber in motor oil.

relatively light having small nuclear collision cross section and hence the nuclear stopping would be insignificant.

From the figure, it can be also noted that the hardness for irradiated composites increase at irradiation dose of 30 kGy according to the crosslinking phenomenon, which is affected by electronic stopping but decrease at 50 kGy as a result of high degradation level.

Swelling behavior

Figures 6 and 7 show the effect of partial replacement of NR with RRP on the swelling behavior of NR/RRP blends in ASTM motor oil and fluid oil, respectively, for 7 days. It can be noted that swelling percentage decrease with increasing RRP content in the blend. This observation is due to the presence of crosslinking rubber particles and other ingredients in RRP, which could limit the penetration of solvents into the blends particularly at higher content of RRP.[26] The swelling percentage decreases dramatically after adding MA in NR/RRP blends because swelling resistance of NR/RRP filled with MA may be correlated to the ability of the chemical to form a protective layer at the interphase, which prevents the diffusion of solvent molecules into NR/RRP.[27] The nature of the fluids and the crosslink density of the polymer are the main parameters, which are controlling the degree of swelling, as described by Ellis and Welding.[28] On the other hand, introduction of GF into blend also increases the hydrophobicity of the blends in ASTM motor oil and fluid oil, hence decreasing the swelling percentage with increasing GF content (Fig. 8).

Swelling resistance or swelling index is a good indication of the extent of crosslinking. It can be noted that the extent of swelling is an inverse function of the crosslinking. This means that the crosslinking increases with decreasing swelling index (Table III). In this table, the swelling index decreases with increasing RRP content in NR/RRP blends as mentioned before.

Figure 9 exhibits the effect of GF and irradiation dose on the swelling index of the NR/RRP/MA (50/50/5) wt % blend. The swelling index increases with increasing GF content and decreasing irradiation dose except for 50 kGy, which is the highest degradation level.

Thermal gravimetric analysis

Thermal degradation curves for NR, RRP, NR/RRP/MA (30/70/5) wt % with and without GF and radiation are shown in Figure 10. The figure shows that, for both NR and RRP, the initial decomposition temperature started at 181 and 185°C, respectively. It can be seen that at a particular temperature, the weight

TABLE III
Effect of RRP Content on the Swelling Index of Unirradiated Blend

NR/RRP	Swelling index
70/30	0.2169
60/40	0.2029
50/50	0.1764
40/60	0.1459
30/70	0.1207

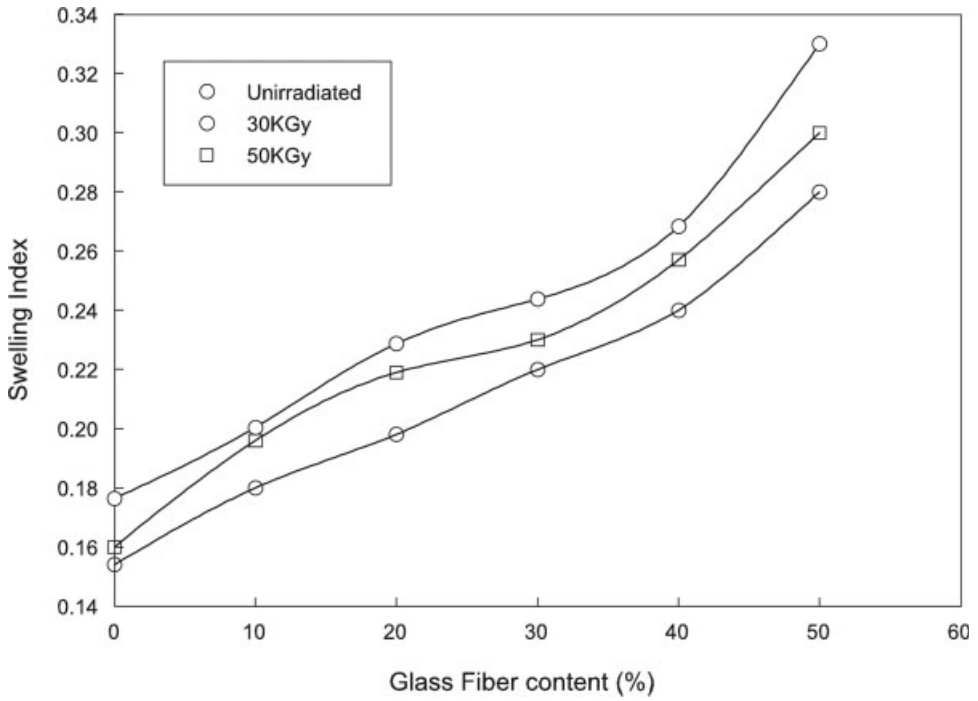

Figure 9 Effect of fiber glass on the swelling index of NR/RRP/MA (50/50/5) wt % composites at different irradiation doses.

loss for pure RRP is lower than that of NR, indicating that the RRP incorporated provides thermal stability to the copolymer matrix and hence the thermal stability of NR is lower than that of RRP. From the TGA thermogram for NR/RRP/MA (30/70/5) wt %, it can be noted that, mixing NR/RRP and the addition of 5% MA to the blend provide shift of TGA curve and also showed difference of onset temperature from 181 and 185°C for NR and RRP, respectively, to 237°C. This result indicates that the compatibility and interfacial bonding increased by mixing NR/RRP and the addition of MA to the blend. It shows that the thermal stability of NR/RRP/wt % (30/70/5) is higher than NR and RRP up to temperature of ≈ 385°C but above that the weight loss of NR/RRP/MA (30/70/5) wt % is higher than that of RRP up to ≈ 480°C, because incorporation of RRP in this range provides more crosslinking and more thermal stability. TGA curve for NR/RRP/MA/GF (30/70/5/50) wt % shows that introduction of 50 wt % GF into the blend produces a composite with high thermal stability. The curve shows that the degradation temperature of 50% weight loss for NR/RRP/MA (30/70/5) wt % and (NR/RRP/MA/GF) (30/70/5/50) wt % are 404 and 581°C, respectively. Therefore, the incorporation of GF into the composite plays an important role for improving the thermal stability of a composite. Exposing the same composite to 50 kGy irradiation dose reduces the thermal stability of composite (Fig. 10), because some degradation occurred when the composite is exposed to 50 kGy as mentioned before in mechanical properties.

Scanning electron microscope

Figures 11–14 show the SEM comparison of tensile fracture surfaces NR, RRP, RRP/NR, RRP/NR/MA, and RRP/NR/MA/GF unirradiated and irradiated compounds at 200× magnification. The micrographs of unirradiated RRP in Figure 11(a) show a rough sur-

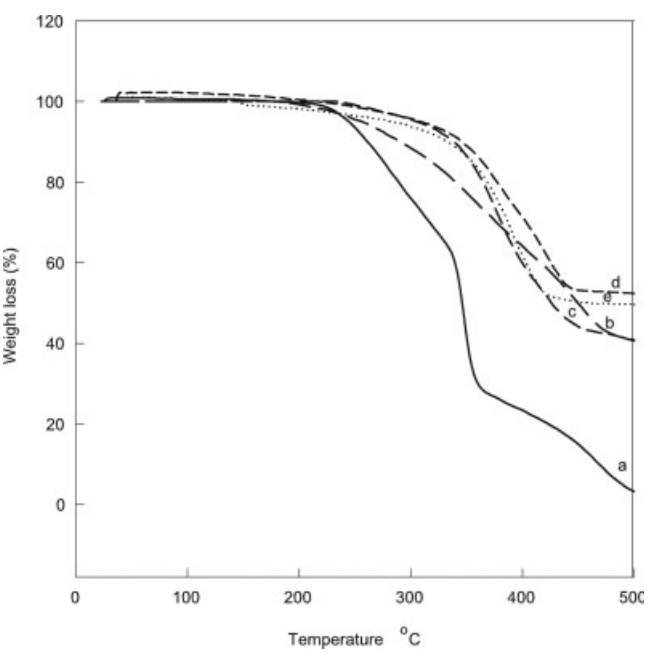

Figure 10 Thermogravimetric analysis (TGA)curve for (a) NR, (b) RRP, (c) NR/RRP (30/70), (d) NR/RRP/GF (30/70/50), and (e) irradiated NR/RRP/GF (30/70/50).

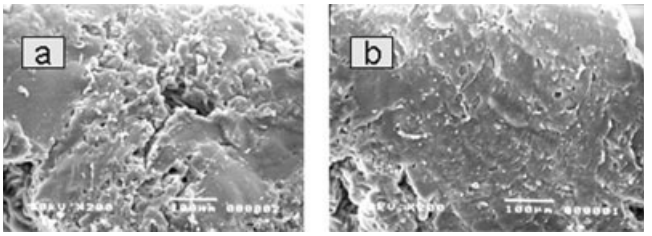

Figure 11 SEM images of (a) nonirradiated RRP and (b) irradiated RRP.

face with many holes or loose RRP. This indicates that during the reclamation process, the molecular chains severely break down. Irradiated RRP in Figure 11(b) exhibits relatively smooth surface, which indicates that the crosslinking occurred between the components of RRP as a result of radiation. The effect of partial replacement of NR with RRP on the morphology of the tensile fracture surface of NR/RRP blends is shown in Figure 12(a). It can be seen that the morphology of the blends is changing with the partial replacement of NR with RRP, and it also exhibits many tear lines, and presence of many holes or loose of RRP on the failure surface (as a result of detachment of RRP from NR matrix) indicates a weak RRP–rubber matrix interaction. These micrographs explain why the tensile strengths decrease with increasing RRP loadings. The micrograph in Figure 12(b) reveals that the morphology of the irradiated NR/RRP (70/30) blend exhibits relatively smooth fracture plane. The morphology of the surface of NR/RRP/MA blends shown in Figure 13(a) exhibits a smooth surface with many vacuoles and undispersed agglomerates, and disappear in irradiated blends. The SEM of the unirradiated GF/NR/RRP/MA (50/50/50/5)%, numerous voids associated with the debonding and pullout of fibers can be readily seen in the fractographs, moreover, crazes are also evident in some areas of the matrix. Some GFs are firmly adhered to the matrix because the MA functional group improves adhesion between GF and other component percent, as mentioned before.

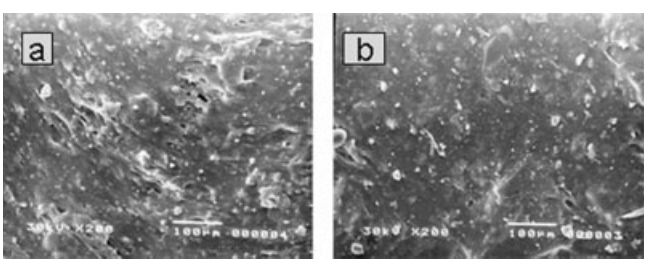

Figure 12 SEM images of (a) nonirradiated RRP/NR and (b) irradiated RRP/NR.

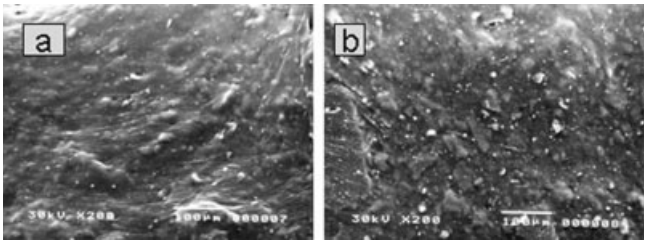

Figure 13 SEM images of (a) nonirradiated RRP/NRL/MA and (b) irradiated RRP/NRL/MA.

It is apparent that the number of voids associated with the pullout of particles is significantly reduced in the irradiated SGF/NR/RRP/MA (50/50/50/5)% (Fig. 14), because a strong bonding developed between irradiated matrix and GFs, due to the formation of crosslinks between the molecules in the rubber chains by e-beam.

CONCLUSIONS

The mixing of RRP with maleated NR and GF in different ratios was achieved using open mill at a temperature of about 70°C.

The tensile strength gradually increases with increasing GF content for nonirradiated composites. The similar trend was found for irradiated composites SGF/NR/RRP/MA (50/50/50/5)%, where the tensile strengths increased by increasing the irradiation doses.

The hardness increases with increasing fiber content. It was also found that the hardness for irradiated composites increase at irradiation dose 30 kGy according to the crosslinking phenomenon, which is affected by electronic stopping but decrease at 50 kGy as a result of high degradation level.

Swelling percentage decrease with increasing RRP content in the blend; also, introduction of GF into blend increases the hydrophobicity of the blends in motor and fluid oils.

The swelling index increases with increasing GF content and decreasing irradiation dose except for 50 kGy.

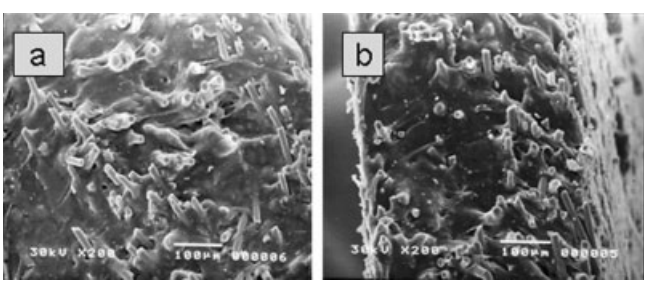

Figure 14 SEM images of composites for (a) unirradiated NRL/RRP/MA/50% glass fiber and (b) irradiated NRL/RRP/MA/50% glass fiber.

The incorporation of GF into the composite plays an important role in improving the thermal stability of a composite.

SEM micrographs also showed the good adhesion between the GF and polymeric matrix after exposure to e-beam.

REFERENCES

1. Hong, C. K.; Isayev, A. I. J Elastic Plast 2001, 33 47.
2. Ishiaku, U. S.; Chong, C. S.; Ismail, H. Polymer Test 1999, 18 621.
3. Jacob, C.; De, P. P.; Bhowmick, A. K.; De, S. K. J Appl Polym Sci 2001, 82, 3293.
4. Jacob, C.; De, P. P.; Bhowmick, A. K.; De, S. K. J Appl Polym Sci 2001, 82, 3304.
5. Mathew, G.; Singh, R. P.; Lakshminarayanam, R.; Thomas, S. J Appl Polym Sci 1996, 61, 2035.
6. Acetta, A.; Vergnaud J. M. Rubber Chem Technol 1981, 54 302.
7. Acetta, A.; Vergnaud J. M. Rubber Chem Technol 1982, 55 961.
8. Mathew, G.; Singh, R. P.; Nair, N. R.; Thomas, S. Polymer 2001, 42, 2137.
9. Wiessner, S.; Wagenknecht, U.; Zichner, M.; Michael, H.; Heinrich, G. Presented at the Proceedings of the 21st Annual Meeting of the Polymer Processing Society (PPS-21), Leipzig, Germany, June 19-23, 2005; CDROM e ISBN 3-86010-784-4.
10. van Duin, M.; Machado, A. V. Polymer 2005, 46, 6575.
11. Oliphant, K.; Baker, W. E. Polym Eng Sci 1993, 33, 166.
12. Pramanik, P. K.; Baker, W. E. Plast Rubber Compos Process Appl 1995, 24, 229.
13. Rajalingam, P.; Baker, W. E. Rubber Chem Technol 1992, 65, 908.
14. Younan, A. F.; Ismail, M. N.; Yehia A. A. J Appl Polym Sci 1992, 45, 1967.
15. Van der Pol, J. F. Rubber World 1994, 210, 32.
16. Varghese, S.; Kuriakose, B.; Thomas, S.; Koshy A. T. J Adhes Sci Technol 1994, 8, 235.
17. Geethamma, V. G.; Joseph, R.; Thomas, S. J Appl Polym Sci 1995, 55, 583.
18. Kang, C. K.; Shin, G. S.; Kim B. K. Polymer (Korea) 1991, 15, 456.
19. Kim, B. K.; Kang, C. K.; Shin G. S. Polymer (Korea) 1991, 15 742.
20. Younan, A. F.; Ismail, M. N.; Khalaf A. I. Polym Degrad Stab 1995, 48, 103.
21. Yang, J. In Environmental Applications of Ionizing Radiation; Cooper, W. J.; Curry, R. D.; O'Shea, K. E., Eds.; Wiley: New York, 1998; p 601.
22. Charlesby, A. Atomic Radiation and Polymers; Pergamon: London, 1960.
23. Thomas, E. V. Presented at the Proceedings of the International Symposium on Radiation Vulcanization of Natural Rubber Latex, Japan, 1989; JAERI-M-89-228, 1990, 178.
24. Cowie, J. M. Polymers: Chemistry and Physics of Modern Materials; Billing and Sons: Worcester, GB, 1973; p 283.
25. Lee, E. H.; Rao, G. R.; Mansur, L. K. Mater Sci Forum 1997, 248/249, 135.
26. Mousa, A.; Ishiaku, U. S.; Mohd Ishak, Z. A. Plast Rubber Compos Process Appl 1997, 26, 331.
27. Othman, N.; Ismail, H.; Mariatti, M. Polym Degrad Stab 2006, 91, 1761.
28. Ellis, B.; Welding, G. N. Rubber Chem Technol 1963, 36, 562.