



ORIGINAL ARTICLE

Influence of gamma irradiation on mechanical and thermal properties of waste polyethylene/nitrile butadiene rubber blend



Raouf O. Aly

Department of Polymer Chemistry, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

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Abstract Gamma irradiation radical–radical interaction crosslinking of elastomers and thermo-plastic is a special type of crosslinking technique that has gained importance over conventional chemical crosslinking method as process is fast, pollution free, and simple. In this work a blend polymer, based on waste polyethylene and nitrile butadiene rubber, has been irradiated with gamma-rays, mechanically and thermally investigated at varying NBR content. FTIR and SEM techniques were used in addition to the swelling behavior to emphasize the blend formation. Mechanical properties like tensile strength, elongation at break and modulus at different elongations were studied and compared with those of unirradiated ones. A relatively low-radiation dose was found effective in improving the level of mechanical properties. Differential scanning calorimeter and thermogravimetric analysis were used to study the thermal characteristics of the irradiated polymer. Enhancement in thermal stability has been observed for higher NBR containing blends and via radiation-induced crosslinking up to ≈ 50 kGy.

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1. Introduction

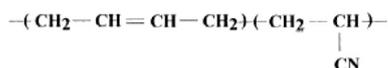
Acrylonitrile–butadiene rubber (NBR) seals are commercially available for more than 50 years because of its low cost, excellent resistance to oil, fuels and greases, and easy processability (Yasin et al., 2002). NBR belongs to the crosslinking type rubber when exposed to high energy radiation. It is well known that the exposure of crosslinking type polymers to radiation provides improved stability and mechanical properties. However to crosslink NBR, high radiation doses are required to reach the desired crosslink density. But at high radiation doses the mechanical properties are adversely affected due to the degradation induced by radiation (Shafy et al., 2011; Clavreul and Pellegrin, 2001). NBR is widely used in oil seals, automotive

E-mail address: raoufokasha@yahoo.co.uk

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hoses and other applications. The acrylonitrile content in commercial nitrile rubber can vary from 25% to 50%. The property of the nitrile rubber is dependent on the acrylonitrile content (Chakraborty et al., 2007). The amount of acrylonitrile content determines the oil resistance of the rubber (Balachandran et al., 2010, 2012). Its use in automotive applications is interesting but the ageing resistance is limited because of the unsaturated backbone of the butadiene (Chakraborty et al., 2007). The chemical structure of NBR is shown below:



Several studies on NBR based nanocomposites have shown that the addition of nanoclay gives a marked improvement in mechanical and barrier properties (Hwang et al., 2004; Kim et al., 2003; Balachandran et al., 2010).

The plastics waste alone is about 10 million tons per year. This is only one fifth of the actual plastics production in Europe. The difference is explained partly by long-term application (automobile industry: 15 years use; building applications: 50 years use), and partly by exports. In order to target specific polymers for recycling research, it is instructive to compare the relative quantities of the main polymer types in the municipal waste stream. In the US, five main types of polymers dominate the stream. The highest polymer waste results from low density polyethylene (LDPE), at 5 million tons per year. High density polyethylene (HDPE) is second, at 4.1 million tons.

The technology of polymer blending has emerged as a useful tool in tailoring polymers to the needs of the end users. According, blending with waste plastics is important both from the point of view of disposal of waste and the reduction in the product cost (Siddique et al., 2008). This work aimed at extending the knowledge of the impact of gamma irradiation on the thermal and mechanical properties of waste polyethylene/NBR blend.

2. Experimental

2.1. Materials

Nitrile-butadiene rubber, under the commercial name of KRY-NAC 4050, was supplied by Bayer, Leverkusen, Germany, with an average acrylonitrile content of 40 wt.%, Mooney viscosity $ML_{1+4}(100\text{ }^\circ\text{C}) 50 + 5$ and density 0.98 g/cm^3 .

2.2. Molding

Sheets of 1 mm thickness were obtained by compressing molding between Holland cloth in clear and polished molds, adjusted beforehand to the melting point temperature of polypropylene at $170\text{--}175\text{ }^\circ\text{C}$ for about 10 min. Pressure of 10 MPa was experienced by the press on the mold surfaces for 5 min. Moldings were then cooled under compression.

2.3. Gamma radiation treatment

Irradiation was carried out at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt. The samples were subjected to gamma radiation (gamma cell type 4000 A, India), in air, at ambient humidity and temperature. The absorbed doses were 50, 75, 100 and 150 kGy at a radiation dose rate of $\approx 4\text{ kGy/h}$.

2.4. Mechanical measurements

Tensile properties of the blends were determined by using Houns Fild computer aided testing machine, UK. The ISO 37-1977 (E) and ISO 34-1975 (E) standards were followed in measuring tensile strength, elastic modulus and elongation at break, respectively. Mechanical properties measurements were carried out on dumbbell shaped specimens of 4 mm width and 50 mm length. Experiments were progressed in triplets and the mean value was determined out of the gained results.

2.5. Differential scanning calorimetry (DSC)

The thermal properties of all composites were investigated by means of the DSC employing a Perkin-Elmer Pyris 1 calorimeter system under constant operating conditions 20 ml/min within the temperature range from ambient to $200\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C/min}$.

2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 system, Japan, and heated within the temperature range $20\text{--}600\text{ }^\circ\text{C}$ at a rate of $20\text{ }^\circ\text{C/min}$, under a controlled dry nitrogen flow of 20 ml/min.

2.7. Infrared spectroscopic analysis

The infrared spectra were performed by using FTIR spectrophotometer, Mattson 100, Unicam, UK, over the range $500\text{--}4000\text{ cm}^{-1}$. The samples were dried in a vacuum oven at $80\text{ }^\circ\text{C}$ for 2 h. A dry constant weight from each blend was ground with 3 mg KBr and then pressed to form transparent discs.

2.8. Swelling measurements

The swelling degree was determined on the basis of equilibrium solvent-swelling measurements in toluene. The samples were submerged in the solvent and after the swelling equilibrium was reached, that means, no change in the weight of the swollen sample was observed, the mass of solvent was determined according to the ASTM D 471. The results were expressed as the mass of solvent absorbed per gram of blend and composite.

2.9. Morphological characterization

An ISM-5400 scanning electron microscope, JEOL, Japan, was used for morphological observation of fracture cross-section samples in liquid nitrogen and coated with gold before testing.

3. Results and discussion

3.1. Elucidation of compounding

Fig. 1. displays the FTIR spectra of unirradiated and irradiated recycled PE and its blends with NBR at various compositions. The hydrocarbon compound is represented by a strong

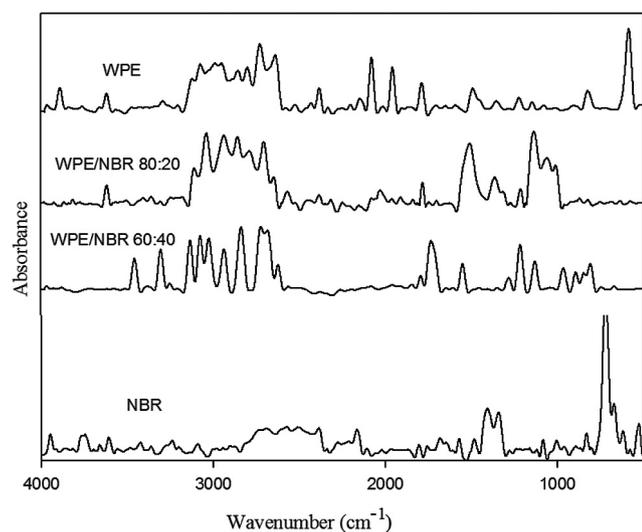


Figure 1 FTIR spectra of WPE, NBR and WPE blended with different feed ratio f NBR.

multiple band near 2940 cm^{-1} and within the interval between 1470 and 1428 cm^{-1} . Such bands correspond to different vibrational modes of the $-\text{CH}_2$ sequences (Hassan et al., 2007). The characteristic band corresponding to the vibrational movement of the methyl $-\text{C}-\text{H}$ of the bond, approximately at 1370 cm^{-1} can also be seen. Additionally, the spectra display other sharp bands of medium intensity within the region $1250-833\text{ cm}^{-1}$. In the given spectrum of NBR, the band at 2330 cm^{-1} is ascribed to alkyl $\text{C}\equiv\text{N}-$ stretching vibrations, whose intensity increases with the NBR content whereas the band at 960 cm^{-1} is due to the $-\text{C}-\text{H}$ wagging motion vibration of butadiene.

Fig. 2 depicts the FTIR spectrum of the blend 20 wt.% NBR, at various radiation doses. The absorption band noticeable near 1713 cm^{-1} , is attributed to the carbonyl group suggesting the changes induced by degradation reactions and ascertaining the type of degradation taking place via the initial irradiation. The spectrum of the sample irradiated at 100 kGy reveals a steady increase in the intensity of the band at 1723 cm^{-1} indicating the formation of a carbonyl group as a result of the production of aldehydes and ketones. The

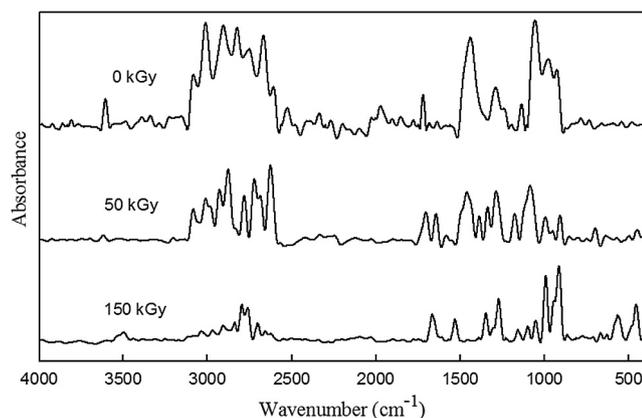


Figure 2 FTIR spectra of WPE blended with NBR (80/20) wt.% at various gamma radiation doses.

post-irradiation changes presumably yield from the interaction of oxygen molecules with the free radicals trapped in the polymer. Such reactions are known to be strongly controlled by the rate of diffusion of oxygen into the polymer (Perera et al., 2004). Nonetheless, the WPE/NBR (80/20) blend shows a very weak unchangeable band at 1723 cm^{-1} with irradiation at 50 and 150 kGy .

3.2. Swelling behavior

Fig. 3 reveals that the rate of toluene uptake was relatively fast in the initial stage up to 2 h thereafter reached an equilibrium state. It can be seen clearly that the swelling percentage increases remarkably as NBR content exceeded 50% . This observation can be illustrated on the basis of the blend microstructure as blend is more rigid and stiff at low NBR content preventing penetration of solvent into the blend. Fig. 4 represents the swelling behavior of the blend (80/20) irradiated up to 100 kGy , notably, the swelling percentage decreases steadily with increasing radiation dose indicating enhancement in gamma irradiation induced-crosslinking. This results in a growing hamper to solvent penetration through the polymer matrix.

3.3. Mechanical properties

The variation of tensile strength (Ts) with the addition of acrylonitrile butadiene copolymer (NBR) to WPE is shown in Fig. 5. It is noticed that the parameter value decreases by increasing NBR content in the unirradiated blend. This can be explained on the fact of that unirradiated NBR is a gum rubber. On other hand, by irradiation at similar NBR content almost higher Ts values were reported with respect to a level off at 50% NBR content. 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 γ irradiation on Ts of NBR/WPE with various compositions at different radiation doses is shown in the same figure; the Ts of the samples increased with the respective increase in radiation dose.

Fig. 6 shows the elastic modulus of the WPE/NBR blends. It can be seen that the elastic modulus of the blends decreases with increasing NBR content. At lower NBR content, the

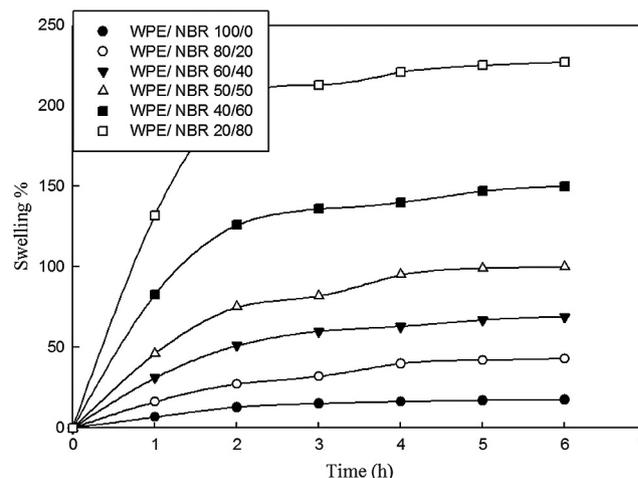


Figure 3 Swelling of unirradiated WPE/NBR blends in toluene.

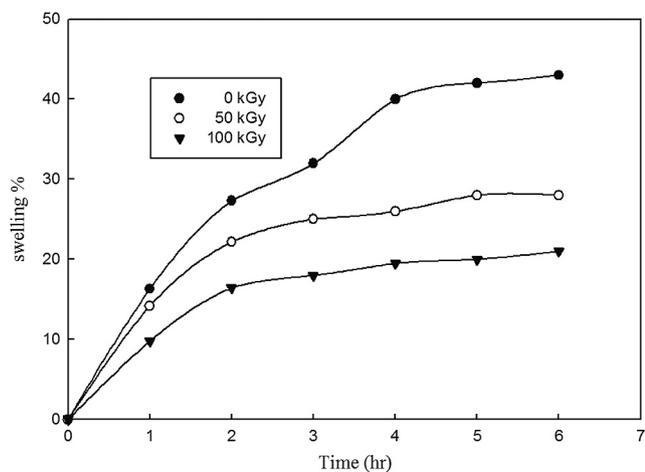


Figure 4 Swelling of WPE/NBR (80/20) wt.% at various gamma irradiation doses.

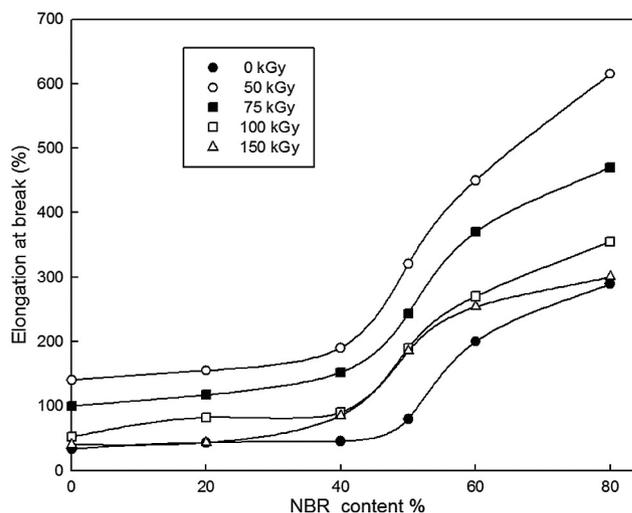


Figure 7 Elongation at bread % of WPE blended with different feed ratios of NBR at various gamma irradiation doses.

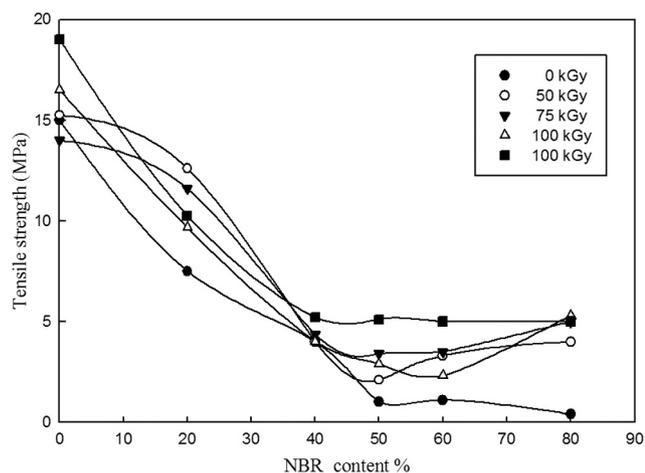


Figure 5 Tensile strength of WPE blended with different fee ratios of NBr at various gamma irradiation doses.

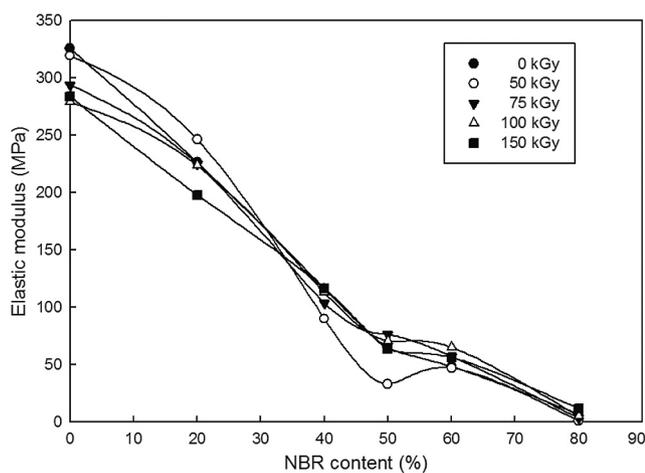


Figure 6 Elastic modules of WPE with different feed ratios of NBR at various gamma irradiation doses.

elastomer phase remains as dispersed particles. Smaller size and uniform dispersion of the dispersed phase contribute to the higher elastic modulus of WPE/NBR blends. As the NBR content further increases, agglomeration and hence particle–particle interaction of the NBR accounts for the observed decrease in elastic modulus of WPE/NBR blends. This is a common observation revealed by many researchers ([Abou Zeid et al., 2008](#); [Abou Zeid, 2007](#)). Apparently, unsystematic behavior at similar radiation dose predominates.

The effect of WPE content on the elongation at break of NBR/WPE blends is shown in [Fig. 7](#). The significant increase in elongation is referred to the increase of NBR content. According to recent theories, the most accepted mechanism for rubber toughening is rubber cavitations, followed by ductile shear yielding ([Ratna, 2005](#)). In rubber-modified plastics, under triaxial tensile stresses, voids can be initiated inside the rubber particles. Once the rubber particles are cavitated, the hydrostatic tension in the material is relieved. This new stress state is favorable for the initiation of shear bands ([Ratna,](#)

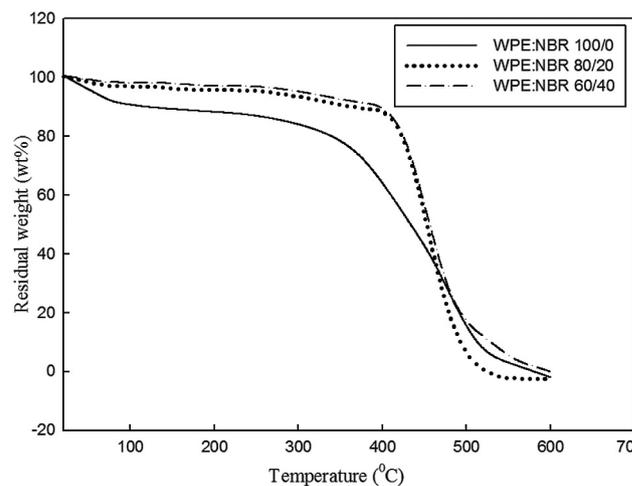


Figure 8 TGA thermograms of WPE/NBR blends at various compositions.

WPE/NBR content%	Dose (kGy)	T_{onset} ($^{\circ}\text{C}$)	$T_{0.5}$ ($^{\circ}\text{C}$)	Charred residue at 600 $^{\circ}\text{C}$ (wt.%)
100WPE	0	113.0	434.3	0
80WPE/20NBR	0	363.4	452.7	0
	50	432	472.0	0
	100	360.6	444.7	0
60WPE/40NBR	0	414.1	455.5	0
	50	418.4	463.5	0
	100	414.0	456.0	0

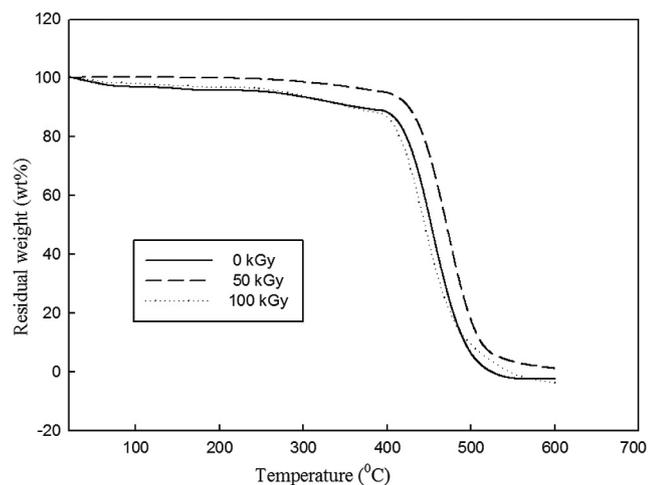


Figure 9 TGA thermograms of WPE/NBR (80/20) wt.% at various gamma irradiation doses.

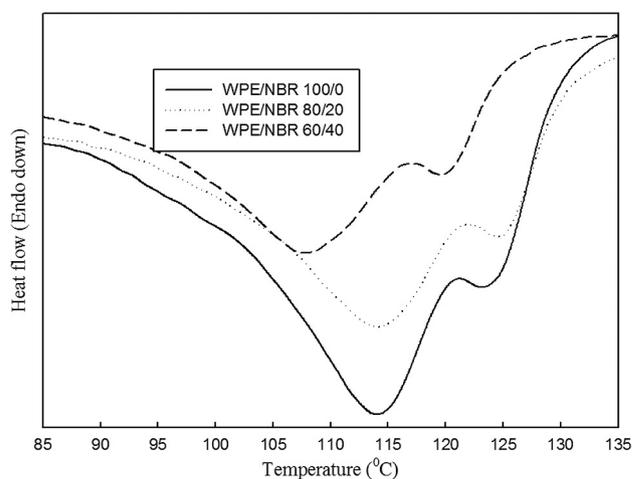


Figure 11 DSC thermographs of unirradiated WPE/NBR blends.

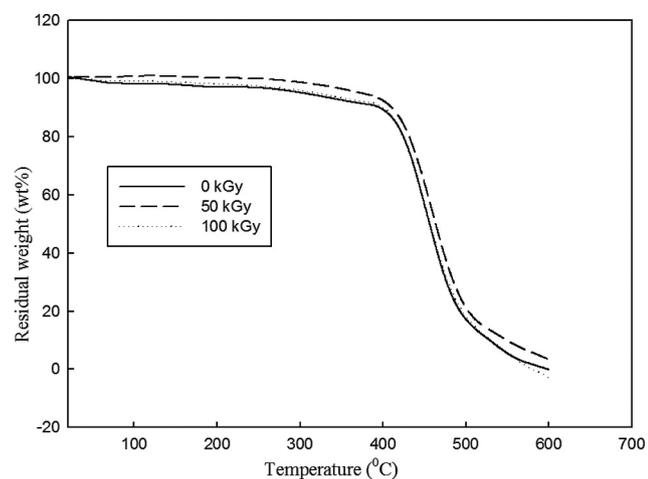


Figure 10 TGA thermograms of WPE/NBR (60/40) wt.% at various gamma irradiation doses.

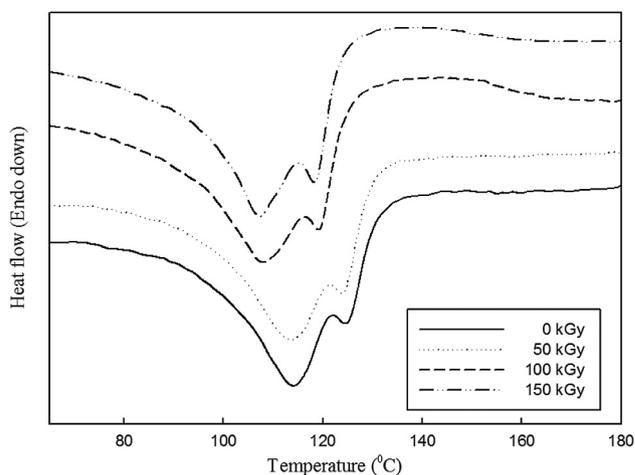


Figure 12 DSC thermographs of WPE blended with NBR (80/20) wt.% at various gamma irradiation doses.

2005; Ratna et al., 2003; Marie et al., 2005). NBR/WPE blend markedly shows initially increase in elongation by the radiation dose 50 kGy, which tends to decrease till the dose of 150 kGy. It is also noticed that elongation at break abruptly increases by irradiation as NBR feed ratio exceeds 50 wt.%. The change in elongation indicates morphological and physical changes in the material. Which have been emphasized by the extracted scanning electron micrograph.

3.4. Thermogravimetric analysis

The TGA thermograms of the unirradiated and irradiated samples are shown in Fig. 8. WPE/NBR blends generally show higher thermal stability than WPE alone and degrade in one step. The two feed ratio 20 and 40 of NBR load in WPE in-

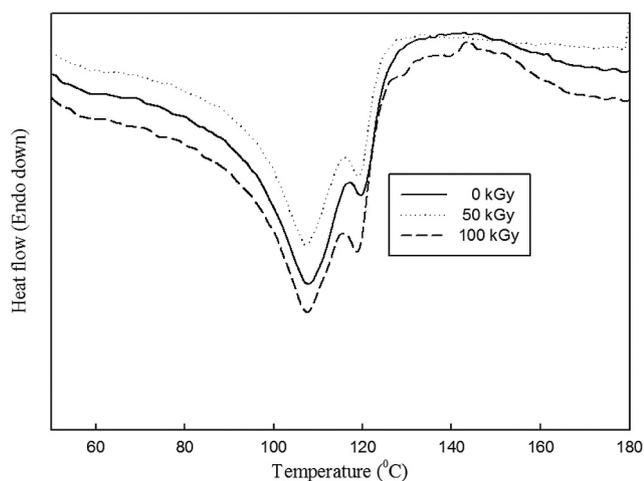


Figure 13 DSC thermographs of WPE blended with NBR (60/40) wt.% at various gamma irradiation doses.

increases the thermal stability of the blend as indicated by the elevation in the onset temperature for degradation. The temperature for 10% mass loss, $T_{10\%}$, was taken as a measure for the onset of degradation and typical values are listed in Table 1. T_{onset} increases from 113 °C for WPE to 363.4 and 414.1 °C for blend with 20% and 40% NBR, respectively. Also the increase in values of $T_{0.5}$ supports the role of NBR in constructing the skeleton of the blend which is markedly accompanied by thermal stability improvement.

Figs. 9 and 10 shows the data obtained by the variation of NBR % content against temperature at the radiation doses 50 and 100 kGy. Remarkably, the irradiated samples at 50 kGy exhibit higher thermal stability in terms of $T_{10\%}$ and $T_{0.5}$ than that of the unirradiated samples as expected. Radiation cross-linking improved the thermal stability at relatively low doses in contrast at higher doses the degradation is predominant.

3.5. Differential scanning calorimetry

Temperatures of the phase transitions for individual polymers, as obtained from the crystalline melting curves recorded by

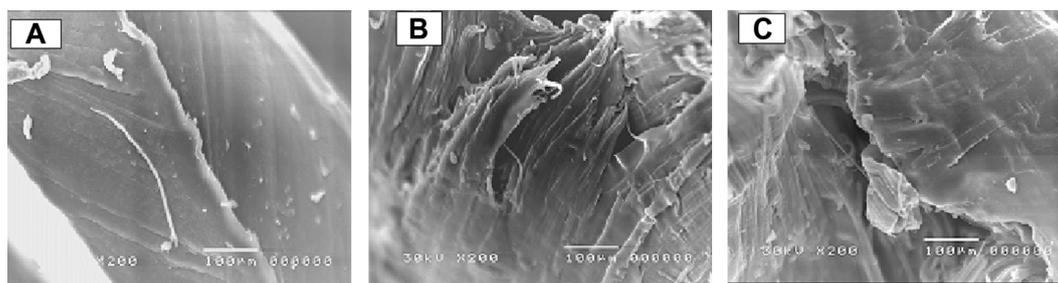


Figure 14 Scanning electron micrographs of unirradiated WPE/NBR blends: (A) 100/0, (B) 80/20 m, (C) 60/40.

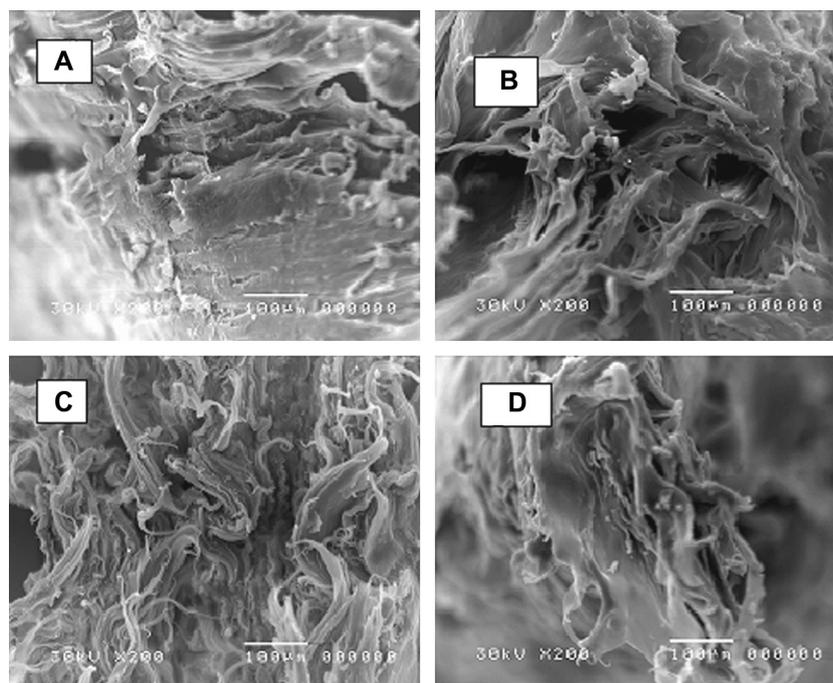


Figure 15 Scanning electron micrographs of WPE/NBR 80/20 blend at various gamma irradiation doses: (A) 0 kGy, (B) 50 kGy, (C) 100 kGy and (D) 150 kGy.

using DSC, are commonly known, which helps to identify specified polymers. In case of polymer blends, the situation is much more complex: the peaks corresponding to the phase transitions of individual components of the blends may shift and overlap each other.

The DSC curves for the two component polymer blends are shown in Fig. 11. The unirradiated sample exhibits a peak with the maximum at T_m , 114.3 °C wide and clearly asymmetric. It is associated with the melting of the crystalline phases of WPE at 117 °C and its asymmetry results from the difference in the melting points of these phases. Obviously, the thermal decreases with the increase in NBR%, as the NBR particles locating in the interlamellar spaces and, cause, the reductions in enthalpy of fusion and degree of crystallinity (Thanisarat et al., 2010). Shoulders in the region 115–125 °C diverse in rPE crystallinity.

Figs. 12 and 13 shows the data obtained by the variation of NBR% content against temperature at the radiation doses 50 and 100 kGy. The increase or decrease in crystallinity of the samples would have some correlation to the oxidation process during irradiation. The oxidation of polymer matrix due to ionizing radiation would cause an increase in chain scission events (Chytiri et al., 2006), which is followed by re-arrangement of the segmented molecules of entangled molecules in the amorphous phase. The segmented molecules would enhance the regularity of rPE, thus resulting in an increase in the degree of crystallinity as well (Hassan et al., 2010).

3.6. Scanning electron microscopy

The morphology of heterogeneous polymer blends depends on blend composition, viscosity of individual components and processing history. Morphology is determined by the melt viscosity ratio and composition. Generally, the least viscous component was observed to form the continuous phase over a larger composition range. The scanning electron micrographs of unirradiated WPE/NBR blends have been extracted and shown in Fig. 14. In the unirradiated WPE/NBR blend, NBR is found to be dispersed as domains in the continuous PE matrix. This is due to the higher melt viscosity and lower content of NBR compared to WPE in the blend. The bigger particle size of the rubber phase with increase in rubber content is attributed to the re-agglomeration or coalescence of the dispersed rubber particles. The occurrence of coalescence at higher concentrations of one of the components.

For irradiated PE/NBR (80/20) blend at different gamma radiation doses, Fig. 15. The fracture surfaces are clearly fibrous with highly stretched regions, characterizing a ductile fracture mechanism with a large macroscopic plastic strain. However, there is a marked difference in the fibrillar appearance, the specimens irradiated with 100 kGy have coarser fibrils, showing that the gamma irradiation influenced the deformation mechanism. This variation has been attributed to an increase in the mechanical strength of the material due to radiation crosslinking. The 150 kGy irradiated PE blend presents a mixed mode of fracture, being more brittle, with smooth areas associated to localized plastic strain regions.

4. Conclusions

The results of this investigation have revealed successful compounding of the blend fraction which has been satisfactorily

elucidated via the FTIR spectra and SEM. In addition, the swelling behavior emphasizes the role of increasing NBR content in lessening the stiffness of the microstructure, the latter has been shown to the radiation-induced crosslinking.

By irradiation tensile strength and elongation at break showed significant improvement, whereas elastic modulus values revealed insignificant variation. It has been found that the increase in NBR content adversely affects the tensile and the elastic parameters. However, exceeding 50% markedly improved the elongation behavior.

The outstanding enhancement in thermal stability has been associated with the NBR content and the radiation-induced crosslinking up to ≈ 50 kGy.

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