

Mechanical Behaviours and Thermal Stabilities of Irradiated Epoxidized Natural Rubber/Polyvinyl Chloride/Carbon Nanotubes Nanocomposites

Mohd Shahrulnizam Ahmad^a, Zurina Mohamad^{a,*}, Chantara Theyv Ratnam^b, Norhayani Othman^a, Roshafima Rasit Ali^c

^aDepartment of Polymer Engineering, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

^bMalaysian Institute for Nuclear Technology Research (MINT), Bangi, 43000 Kajang, Malaysia

^cDepartment of Environment and Green Technology (EGT), Malaysia-Japan International Institute of Technology (MJIT), Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia
 r-zurina@utm.my

The effects of carbon nanotubes addition (nanotube contents and functionalized MWNTs) and also irradiation modification on the mechanical behaviours and thermal stabilities of epoxidized natural rubber (ENR-50)/poly (vinyl chloride) (PVC)/multi-walled carbon nanotubes (MWNTs) nanocomposites were investigated. ENR-50/PVC/MWNTs nanocomposites were prepared by melt mixing in a Brabender Plastigraph at 150 °C with a rotor speed of 50 rpm followed by compression molding at 160 °C. The samples were irradiated in a 2 MeV electron beam (EB) machine at a dose of 200 kGy. The dynamic mechanical properties and glass transition temperature properties of the resulting composites were investigated as a function of MWNTs contents, functionalized MWNTs, and irradiation dose. The storage modulus and glass transition temperature (T_g) increased by increasing nanotube content (0 to 8 phr) at 0 kGy and further increased after being irradiated with 200 kGy. Moreover, this is inversely proportional to loss modulus and can be seen that loss modulus decreased with the addition of nanotube content. In the aspect of functionalization effects, MWNTs-COOH recorded higher T_g at 0 kGy and MWNTs-OH at 200 kGy. However, results for storage modulus by the effect of functionalization totally dropped as compared with ENR-50/PVC and ENR-50/PVC/MWNTs blends. This showed that the storage modulus is not proportional to the increase of T_g and also the loss modulus.

1. Introduction

The blending of different polymers has become a technologically important field because it can generate new materials with better specific properties (Ratnam et al., 2001a). Hence, the blending of polyvinyl chloride (PVC) and epoxidized natural rubber (ENR) has become an interesting investigation by many researchers. ENR forms miscible blends with PVC (Raju et al., 2008), in which PVC has properties which are high tensile strength and good chemical resistance and ENR will give a permanent plasticizer to PVC, produces good tear strength and improves resistance against hydrocarbon oils. It was also reported that PVC and ENR form self-cross linkable blends (Perera et al., 2000). ENR/PVC blends are frequently utilized in footwear, cellular sports surfaces, hose lining and covers, conveyer belt covers, and cable jackets (Ratnam and Zaman, 1999). The blends are also expected to be excellent choices for usage in automotive interior components like gaskets and o-rings, which are subject to higher temperatures and dynamic movement.

In order to enhance the properties of the blends between ENR and PVC, carbon nanotubes (CNTs) and irradiation modification have been introduced by some researchers, nowadays. According to Sahoo et al. (2010), the presence of carbon nanotubes can improve the properties of polymer composites including tensile strength, toughness, glass transition temperature, electrical conductivity, thermal conductivity, and others.

Ratnam et al. (2015) claimed that the addition of CNTs caused a decline in tensile strength (T_s) and modulus 100 (M100) of ENR/PVC due to poor dispersion of CNTs in the polymer matrix. However, upon electron beam

irradiation (EB irradiation), the nanocomposites showed a higher value of tensile strength (Ts) and modulus 100 (M100) as compared to the neat ENR/PVC blends

Although CNTs possess a great challenge which is non-uniform dispersion, this study investigated the effect of multi-walled carbon nanotubes (MWNTs) with their functionalized and crosslinking by EB irradiation. The functionalization can improve the solubility and processibility of the polymer composite. Furthermore, a functionalized nanotube might have mechanical or electrical properties that are different from those of the unfunctionalized nanotube (Sinnott, 2002).

2. Preparation and Characterization

The 50 mol % epoxidations of epoxidized natural rubber (ENR-50) used in this investigation, which had a specific gravity of 1.03, were purchased from the Malaysian Rubber Board. K-65 polyvinyl chloride (PVC) was purchased from P.T. Asashimas Chemical in Anyer, Indonesia. Multiwalled carbon nanotubes (MWNTs), carboxylated carbon nanotubes (MWNTs-COOH), and hydroxylated carbon nanotubes (MWNTs-OH) with typical diameters of 10 to 20 nm, lengths of 10 to 30 μm , specific surface areas of 200 to 350 m^2/g , and 95 % purity were bought from Nanostructured and Amorphous Materials Inc. in Texas, USA. Pre-mixing of unfunctionalized MWNTs and their functionalized with PVC were first mixed together in a high-speed mixer at room temperature for 5 mins to create the composites. In a Brabender Plastigraph, Model W 50 E-3 Zones PL2100-3, melt blending of pre-mixed PVC/MWNTs and ENR-50 was carried out for 10 mins at 150°C and 50 rpm rotor speed. The MWNT is varied at 0 and 8 phr, and the mix of ENR-50 and PVC is kept at 50/50 wt %. For the purpose of creating the testing samples, the composites were molded. Using a 2 MeV electron beam accelerator, Model EPS 3000 (Cockroft Walton), all of the samples were exposed to radiation at doses of 200 kGy. Acceleration energy, 2 MeV; beam current, 5 mA and dosage rate, 50 kGy for each pass are parameters that are being used to irradiate the samples. Using a Perkin-Elmer DMA-7e apparatus in the temperature/time scan mode with a parallel plate attachment, a dynamic mechanical analysis was carried out. The experiment was performed between -90 and 180 °C at a heating rate of 10 °C min⁻¹ and a frequency of 1 Hz. The sample sizes were 2.5 mm in thickness and 10 mm in diameter (Ratnam et al., 2001b).

3. Results and discussion

3.1 Dynamic mechanical analysis

Dynamic mechanical analysis is a proposed method for examining the mechanical properties of polymers and polymer composites. A technique where temperature, time, or oscillation frequency are used to control the sample's storage and loss moduli under an oscillating load. The loss tangent ($\tan \delta$) is the proportion of the loss modulus to the storage modulus. As the molecular movements within the polymer change with temperature, the moduli typically change as well. When a polymer is heated through the glass transition area, its storage modulus rapidly declines while its $\tan \delta$ and loss moduli reach their maximum values. The glass transition temperature (T_g) is determined by taking the greatest peak of $\tan \delta$. Tables 1 and 2 show the results as a function of MWNT content and radiation dose.

Table 1: DMA data for irradiated ENR-50/PVC/MWNTs nanocomposites at 0 kGy of irradiation dose

	Glass Transition Temperature (°C)	Tan δ ($\times 10^{-3}$)	Storage Modulus (MPa)	Loss Modulus (MPa)
ENR-50/PVC	27.03	440	76.1	17.1
ENR-50/PVC/8 MWNTs	29.95	367	96.8	16.3
ENR-50/PVC/8 MWNTs-COOH	32.05-66.65	380-386	43.2	6.90
ENR-50/PVC/8 MWNTs-OH	28.18-61.21	334-336	42.5	10.9

Table 2: DMA data for irradiated ENR-50/PVC/MWNTs nanocomposites at 200 kGy of irradiation dose

	Glass Transition Temperature (°C)	Tan δ ($\times 10^{-3}$)	Storage Modulus (MPa)	Loss Modulus (MPa)
ENR-50/PVC	27.33	431	52.6	12.1
ENR-50/PVC/8 MWNTs	44.46	427	110.0	9.0
ENR-50/PVC/8 MWNTs-COOH	52.24	330	45.4	6.0
ENR-50/PVC/8 MWNTs-OH	57.46	272	32.3	4.2

It can be seen clearly that the T_g becomes higher when the incorporation of MWNTs and their functionalization. This could be attributed to the effect of MWNTs as filler that made the nanocomposites became stiffer and

glassier. These values of T_g increased correlated to the decline of the peaks $\tan \delta$ and loss modulus. Otherwise, the increase in values of storage modulus also can be observed by the incorporation of unfunctionalized MWNTs, but not for functionalized MWNTs at 0 and 200 kGy. Ratnam et al. (2001b) explained that the addition of unfunctionalized MWNTs and irradiation modification could help in microstructural changes and also induced crosslinking among the polymer matrix and also MWNTs as the filler.

The effect of MWNT concentration at 0 (Figure 1(a)) and 200 kGy (Figure 1(b)) of irradiation dosage, on the temperature dependence of the storage modulus and $\tan \delta$ of the ENR-50/PVC are depicted. As hypothesized, as the content of nanotubes increased, the storage modulus and glass transition temperature increased (0 phr to 8 phr). This is because the increased MWNT loading results in a higher level of crosslinking. The addition MWNTs can cause the increase of crosslinking density in elastic components by the aperture of oxirane ring of epoxy group of ENR (Sahakaro, 2017) and also more heat required to transform the nanocomposites from glass to rubbery. Ma et al. (2010) also claimed that carbon nanotube (CNT) is the stiffest and strongest material on this earth; Young's modulus of CNT has recorded up to 1.2 TPa and tensile strength, 50-200 GPa. As a result, CNTs can be used as an ideal reinforcing agent for high-performance polymer composites (Sahoo et al., 2010), which also can induce crosslinking in the polymer matrix.

Figures 1(a) and (b) show that the stiffening impact of MWNTs enhanced the storage modulus of ENR-50/PVC/MWNT nanocomposites at 8 phr nanotube content in comparison to its blend. This may be explained by the fact that carbon nanotubes are present, which also allow the polymer matrix to support a high modulus value. Additionally, there will be a dramatic peak in the transition area if the molecular connection between the polymer matrix is significant and the impact of the interchain chemical heterogeneity is minimal (Ratnam et al., 2001c). However, due to the decrease in stiffness of the nanocomposites, storage modulus rapidly decreases at the glass transition temperature (T_g) zone. With the addition of 8 phr of nanotube content at 0 kGy and subsequently increased after irradiation at 200 kGy, the peak of $\tan \delta$ is slightly shifted to a higher temperature (Figures 1(a) and (b)). This demonstrates that the addition of nanotubes and irradiation-induced crosslinking, whereby crosslinking has the predominant influence, raises the T_g of the nanocomposites. In other words, the segmental mobility of the matrix chains is blocked by MWNTs and irradiation-induced crosslinking. When incorporating carbon nanotubes into polymers, Jin et al. (2001) made a similar observation of poly (methyl methacrylate) (PMMA). The study reported that the addition of carbon nanotubes greatly raised the storage modulus of PMMA nanocomposites at high temperatures and also increased the T_g of nanocomposites. As the inclusion of MWNTs might be associated with the improvement of the irradiation-induced crosslinking efficiency by MWNTs, the lowering of peak loss modulus is coupled with the enhancement in the storage modulus and also $\tan \delta$.

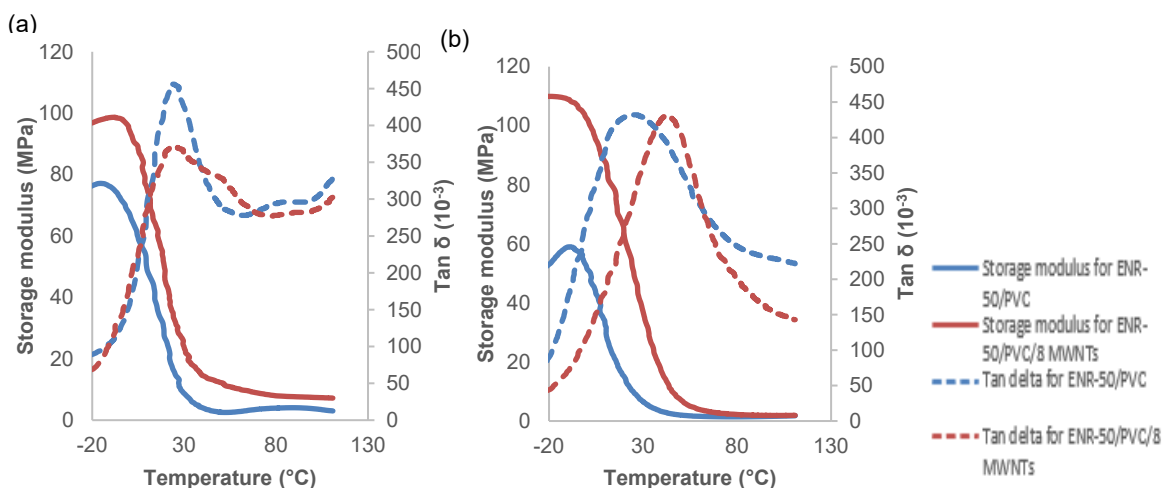


Figure 1: Effect of nanotube content of MWNTs on the temperature dependence of $\tan \delta$ and storage modulus of 50/50 ENR-50/PVC blends; (a) 0 kGy and (b) 200 kGy irradiation doses

The loss modulus peak diminishes with increasing nanotube content and irradiation dose, as demonstrated in Figures 2 (a and b). This demonstrates a typical generic phenomenon: for light rubbers, damping diminishes as crosslinking is increased. Figures 1(a) and 1(b) show a progressive drop in the $\tan \delta_{\max}$ with increasing nanotube concentration and radiation exposure. This may be related to the microstructural alterations brought on by the crosslink formation as a result of the increase of nanotube content and irradiation-induced crosslinking (Ratnam et al., 2001b). This can be explained that irradiation modification especially; can initiate ionization and excitation

of electrons in the polymer matrix and as a consequence, there are some changes in the polymer structure. $\tan \delta$ is a measurement of the energy dissipated as heat (a material's viscous response) to the maximum energy stored in the material (a material's elastic response) throughout the period of an oscillation. The observed trend in the $\tan \delta_{\max}$ is caused by the constant increase in storage modulus, which is accompanied by a continuous decrease in the loss modulus with the increase in nanotube concentration as well as irradiation dose. Research PVC/ENR Blend: Dynamic Mechanical Analysis by Ratnam et al. (2001b) can be used to support this evidence. The loss factor, often known as the damping behavior, is very sensitive to changes in cross-linking density. Therefore, it is reasonable to assume that the chain segments in the glass transition area of irradiated ENR are more constrained than those in the unirradiated ENR. This might be related to the microstructural alterations brought on by the irradiation-induced crosslink (Ratnam et al, 2001b).

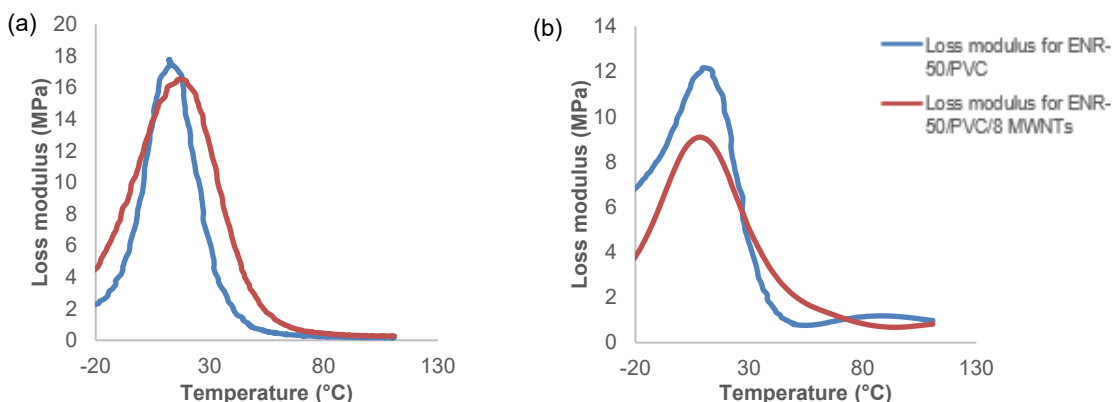


Figure 2: Effect of nanotube content of MWNTs on the temperature dependence of loss modulus of 50/50 ENR-50/PVC blends; (a) 0 kGy and (b) 200 kGy irradiation doses

Figures 3 and 4 illustrate how the functionalization of MWNTs alters the temperature dependence of the storage modulus, $\tan \delta$, and loss modulus of ENR-50/PVC and its nanocomposites.

Figure 3 depicts the impact of functionalized MWNTs on the temperature dependence of the storage modulus and $\tan \delta$ of the ENR-50/PVC at 0 (Figure 3(a)) and 200 kGy (Figure 3(b)) of irradiation dosage. When 8 phr functionalized and unfunctionalized MWNTs were added, the peak of the $\tan \delta$ of the unirradiated nanocomposite (0 kGy) decreased in intensity, indicating that the nanotubes increased the interaction of the nanocomposites. Again, this might be explained by the microstructural alterations brought on by the crosslink production caused by irradiation-induced crosslinking. Comparing functionalized nanocomposites to unfunctionalized nanocomposites, there is no apparent change in T_g . The good interaction between the nano clay and matrix and the self-crosslinking of the ENR component, which have less of an impact on the restriction on the mobility of the polymer chain and less of an impact on shifting the T_g of the nanocomposite, are responsible for the increased gel content of unirradiated nanocomposite with functionalized MWNTs. ENR's crosslinking to another monomer was lowered as a result of this self-crosslinking.

The peak of $\tan \delta$ and storage modulus of irradiated ENR-50/PVC blends, MWNTs, MWNTs-COOH, and MWNTs-OH nanocomposites are shown in Figure 3(b) as functions of temperature. Following the sequence of ENR-50/PVC blends, MWNTs nanocomposite, followed by MWNTs-OH and MWNTs-COOH nanocomposite, the $\tan \delta$ peaks are shifted to the higher temperature. The glass transition temperature, T_g , has increased as a result of the good contact between functionalized MWNTs and the matrix in nanocomposite materials combined with the presence of irradiation-induced crosslinking. The existence of this irradiation-induced crosslinking also has increased the restriction of polymer chain mobility. In addition, it is thought that the bonding of -OH in the polymer matrix is related to the greater T_g of MWNTs-OH. The nanotube's surface contains -COOH and -OH groups, which facilitate the attachment of organic or inorganic substances and are essential for solubilizing nanotubes. Covalent functionalization of CNTs with ester aids in crosslinking of CNTs as well (Sahoo et al., 2010). There are also some several reports on the connection between the crosslink density and the T_g , such as Ratnam et al (2001c). According to the study, the incorporation of nanotube components could lead to the establishment of intermolecular networks, which could increase crosslink density. Thus, a decrease in the $\tan \delta$ peak, the peak of the loss modulus, and shift of the T_g to the higher are also observed.

However, it is evident that the storage modulus maxima for functionalized MWNTs (COOH and OH) at 0 and 200 kGy irradiation dosage are completely dropped when compared to unfunctionalized MWNTs

nanocomposites and ENR-50/PVC blends (Figures 3(a) and 3(b)). This demonstrated that the loss modulus and $\tan \delta$ enhancement are not proportional to the storage modulus. This implies that functionalized MWNTs reduce the size of the network structure, explaining the decrease in storage modulus. The broadening of the $\tan \delta$ peak caused by the addition of functionalized MWNTs lends even more support to this idea. The varied segmental environment may indicate microheterogeneity based on the wider damping peaks. This demonstrates how the chemical structure of functionalized MWNTs varies. These nanocomposites exhibit increased crosslinking densities and also good interaction between the nanofiller and polymer matrix, as evidenced by the decreased storage modulus for unirradiated and irradiated functionalized MWNTs. Ratnam et al. (2001a) also reported that the storage modulus dropped by incorporating trimethylolpropane triacrylate (TMPTA) on the ENR/PVC blend with the same evidence.

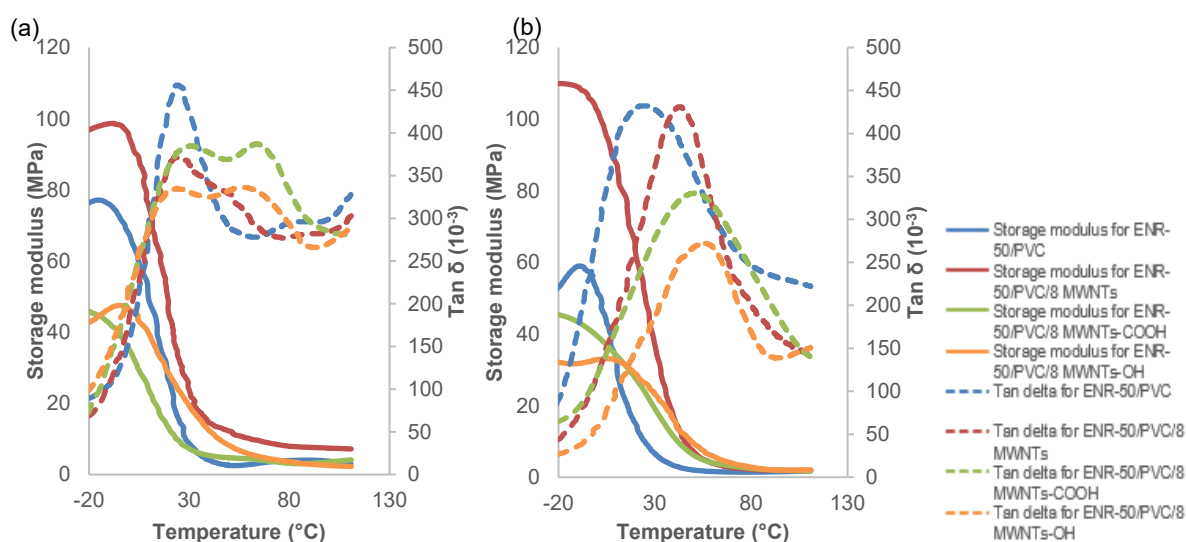


Figure 3: Effect of functionalization of MWNTs (8 phr) on the temperature dependence of $\tan \delta$ and storage modulus of 50/50 ENR-50/PVC blends; (a) 0 kGy and (b) 200 kGy irradiation doses

As seen in Figures 4(a and b), the presence of functionalized MWNTs reduces the peak of the loss modulus. When functionalized MWNTs are added, the $\tan \delta_{\max}$ (Figures 3(a) and 3(b)) similarly shows a progressive reduction. This might be the result of the microstructural adjustments brought about by the crosslink formation via the addition of functionalized MWNTs. The functionalization of MWNTs (COOH and OH) with the matrix in nanocomposite has enhanced the restriction of the polymer chain mobility, increasing the glass transition temperature, T_g , as a result.

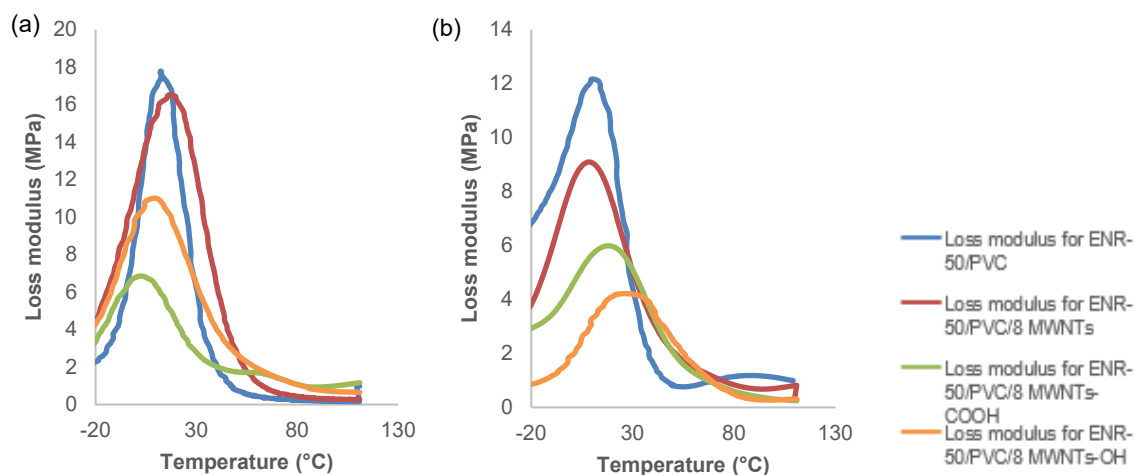


Figure 4: Effect of functionalization of MWNTs (8 phr) on the temperature dependence of loss modulus of 50/50 ENR-50/PVC blends; (a) 0 kGy and (b) 20 kGy irradiation doses

4. Conclusion

The discussion above makes it abundantly evident how crucial nanotube contents and functionalized MWNTs are really important in enhancing the characteristics of ENR-50/PVC blends during irradiation. Results show that irradiating a miscible ENR-50/PVC blend system can maximize enhancement in ENR-50/PVC characteristics under the current conditions. With the addition of 8 phr of nanotube content at 0 kGy and further increased after irradiation at 200 kGy, the storage modulus improved and $\tan \delta$ significantly shifted to a higher temperature. Moreover, the loss modulus decreased with the incorporation of MWNTs and also irradiation dose. In term of functionalization effects, the peak of $\tan \delta$ reduced in intensity with the addition of 8 phr unfunctionalized and functionalized MWNTs (0 kGy) which is correlated to the interaction of nanotubes with polymer and also induce crosslinking in nanocomposites. At 200 kGy, the Tg of functionalized MWNTs increased as compared to the ENR-50/PVC blend and unfunctionalized MWNTs. With the addition of functionalized MWNTs, the peak of the loss modulus decreased. This may be attributable to the functionalization of MWNTs increasing the restriction of polymer chain mobility and raising the glass transition temperature, Tg. Therefore, in order to maximize the beneficial effects of irradiation, some parameters, such as nanotube contents and functionalized MWNTs, can be taken into account. It is also been clear that these effects have a role in improving the miscibility of the ENR-50/PVC blend.

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