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EFFECT OF BLENDING TEMPERATURE ON THE MECHANICAL PROPERTIES OF PVC/ENR BLEND UPON IRRADIATION

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Abstract

Poly (vinyl chloride) / epoxidised natural rubber blends were prepared with a Brabender plasticorder at 140, 150, 160, 170 and 180°C mixing temperatures. They were mixed at 50 rpm rotor speed for 10 min. The blends were irradiated with doses ranging from 0-200 kGy. Changes in tensile strength, modulus at 100% elongation, gel fraction and damping properties (tan δ) of the blends with increasing mixing temperatures and irradiation doses were investigated. In general, it was observed that the mixing temperature is important in maximizing the positive effect of irradiation. Results revealed that a readily miscible blend enjoy maximum benefit from irradiation meanwhile irradiation impart miscibility to a partially miscible PVC/ENR blend. The enhancement in blend properties is believed to be attributed by the irradiation-induced crosslinking along with irradiation-induced interaction between the polymers. The radiation-induced degradation found to be prominent at higher doses for blend that has undergone excessive thermal degradation. However evidence did not reveal the specific nature of radiation-induced reaction responsible for the improved interactions of the blends.

Key words: irradiation; irradiation-induced, temperature; blend, doses

INTRODUCTION

High-energy irradiation (gamma or electron beam) is a well–known technique for the modification of polymers [1-4]. Recent studies by Ratnam and Zaman [5-9] indicated the effect of electron beam irradiation in enhancement of PVC/ENR blend properties. Earlier work on PVC/ENR blends by Nasir and Ratnam [10,11] shown the need of using suitable mixing conditions to attain optimum blend properties. It has been subsequently reported that mechanical properties of PVC/ENR are greatly influenced by the mixing parameter [12]. Blends of epoxidised natural rubber with 50% epoxidation level, ENR 50 and PVC were found to be miscible at any blend ratio if suitable mixing conditions are employed [13,14].

Apparently, the blending conditions found to be prime important in controlling the properties of the blend. In relation to modification of polymer blends by irradiation, attempts have been made to crosslink one of two polymers in a completely miscible blend system [15,16]. In the field of immiscible polymer blends, studies have been performed on improving the mechanical properties via overall crosslinking. Blends of polyethylene and elastomers were irradiated to reduce ply separation and to increase the materials' strength and resistance to heat [17,18]. Thus, it is felt important to look into effect of processing parameters such as blending temperature on the final properties of the irradiated PVC/ENR blends as the miscibility of the blend governed by processing parameters which include blending temperature. The prime objective here is to provide more evidence on the radiation-induced reactions in PVC/ENR blends, and hence improved knowledge on such modifications.

MATERIALS AND METHOD

Materials

Epoxidised natural rubber, grade "EPOXYPRENE 50" with 50 % epoxidation level was supplied by Guthrie Polymer Ltd. as a free sample; polyvinyl chloride (PVC) with a 66 k value, grade "MH66, 6519" was purchased from Industrial Resin (M) Ltd. The PVC stabilizer used, tribasic lead sulfate (TS-100M) was purchased from Lonover Scientific Suppliers Ltd., London. They were used as received.

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Formulations

The 50 / 50: PVC / ENR blends were prepared by mixing 50 parts of PVC with 50 parts of ENR50. The recipes are given in Table 1

Table 1. Formulations of 50 / 50 PVC / ENR blend

Material	Formulation (phr)
PVC	50
ENR50	50
tribasic lead sulfate	2

Blend preparations

PVC and the stabilizer were premixed at room temperature in a tabletop high-speed mixer at 1200 rpm for 10 minutes. Melt blending was carried out at 50 rpm rotor speed in a Brabender Plasticorder Model PL 2000 having a mixing cum attachment. The blending was done as follows:

When the desired temperature was reached, ENR was charged into the mixing chamber and mixed for 1 min. The PVC compound was then added, and the blending continued for a further 9 min. In order to study the effect of blending temperature, the mixing was done in temperatures ranging from 140-180°C. Their respective torque-time curves were then recorded.

The blends obtained from the Brabender Plasticorder were then compression molded into 1-mm thick sheets under a pressure of 150 $kgcm^{-2}$ at 150 ^0C for 3 min. The sheets were immediately cooled between two plates of a cold press at 25 ^0C. Dumbbell - shaped test pieces were cut from these sheets in accordance with BS6746.

Irradiation

The molded sheets and dumbbell test pieces were irradiated using a 3 MeV electron beam accelerator at a dose range of 0-200 kGy. The acceleration energy, beam current, and dose rate were 2 MeV, 2 mA, and 20 kGy / pass, respectively.

Measurement of tensile properties

The tensile strength (Ts) and Modulus at 100% elongation (M100) were measured on a Toyoseiki model Strograph-RI using a crosshead speed of 50 mm / min. Altogether, eight samples were used for the tensile test and an average of six results was taken as the resultant value.

Gel fraction

The gel fraction was determined by extraction in tetrahydrofuran (THF), at 50 ± 2 °C. The blends were solvent extracted with THF for 16 hours and the extracted samples were dried to constant weight. The gel fraction was calculated as;

gel fraction: $(W / W_0) \times 100$ (I)

where W and W_0 are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis was performed using Perkin Elmer DMA-7e in the temperature / time scan mode with a parallel plate. The measurements were carried out at a heating rate of 10^0C / min. over a temperature range of -50^0C to 120^0C and a frequency of 1 Hz.

RESULTS AND DISCUSSION.

Brabender studies

Brabender studies conducted by several workers [19,20] have shown that data obtained from the measurement of torque can be used to interpret the processing behavior of materials. The significance of the torque-time curves obtained from Brabender studies for ENR/PVC blends [12] and PVC/NBR [21] blends have been well demonstrated.

Fig. 1 shows the variation of mixing torque and with mixing time in the Brabender Plasticorder at temperatures ranging from 140 to 180°C. As observed, the presence of the fusion peak, followed by the stabilization zone and

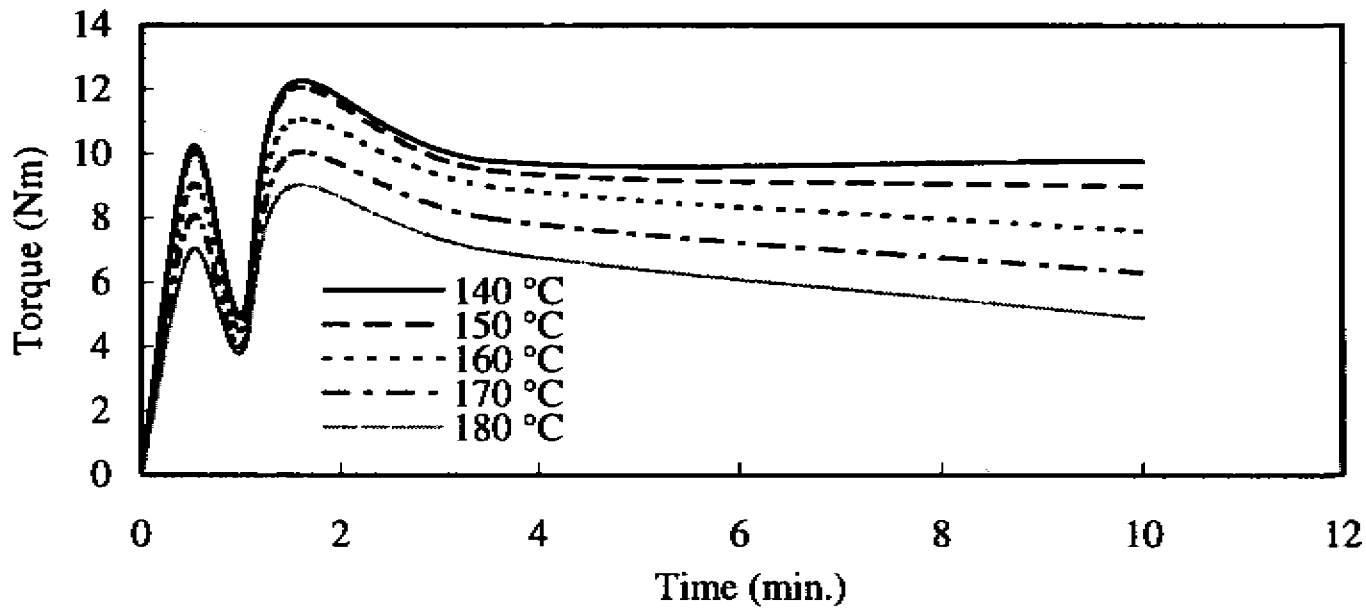

Fig. 1: Plastograms of 50/50 PVC/ENR blends obtained between 140 and 180°C at rotor speed of 50 rpm.

the absence of rising torque, is a clear evidence of successful blending. Apparently, the stabilization zone achieved within the 10 min of mixing time for 140 and 150°C suggests that these temperatures would be suitable to attain good blend. However, the slightly higher torque exhibited for 140°Cmixing temperature could be an indication of inadequate mixing of the polymers. It is also clear from Fig.1 that after the fusion peak, the torque shows gradual decline with increasing temperatures above 150°C. This fall in torque-time curve is attributed to the thermo-mechanical degradation of the blends. The influence of such effects on the properties of the blends upon irradiation will be discussed in the preceding sections.

Tensile properties

Fig. 2 depicts the effect of irradiation on the Ts of PVC/ENR blends prepared at various mixing temperatures. Prior to irradiation, an almost negligible difference in Ts of blends prepared at 140 and 150°C is observed. However, the Ts found to decrease gradually with increasing blending temperature beyond 150°C. This trend of results is believed to be attributed to the thermal degradation of the blends at above 150°C as observed in Brabender torque-time curves.

Figure 2 also indicate a gradual increase in Ts with irradiation dose. This enhancement in Ts is could be due to the radiation-induced crosslinking as reported previously [5-9]. However, it is interesting to note that the blends obtained at 150°C render the best enhancement in Ts upon irradiation. It is also apparent that the blend mixed at 140°C render lower Ts upon irradiation than those obtained at 150°C although their initial Ts values did not differ. These results believed to be attributed to the incomplete mixing and fusion of PVC at 140°C which may had resulted in incomplete miscibility of the blend. This observation is in perfect agreement with Brabender torque-time curve, in which 150°C found to be optimum temperature to attain good blend.

Another interesting trend to note is, the drop in Ts observed for blend prepared at 140°C and 180°C above 100 kGy irradiation dose. The explanations for such observation could be as follows; the initial increase in Ts upon irradiation of blends prepared at 140°C could be attributed to both radiation-induced crosslinking as well as

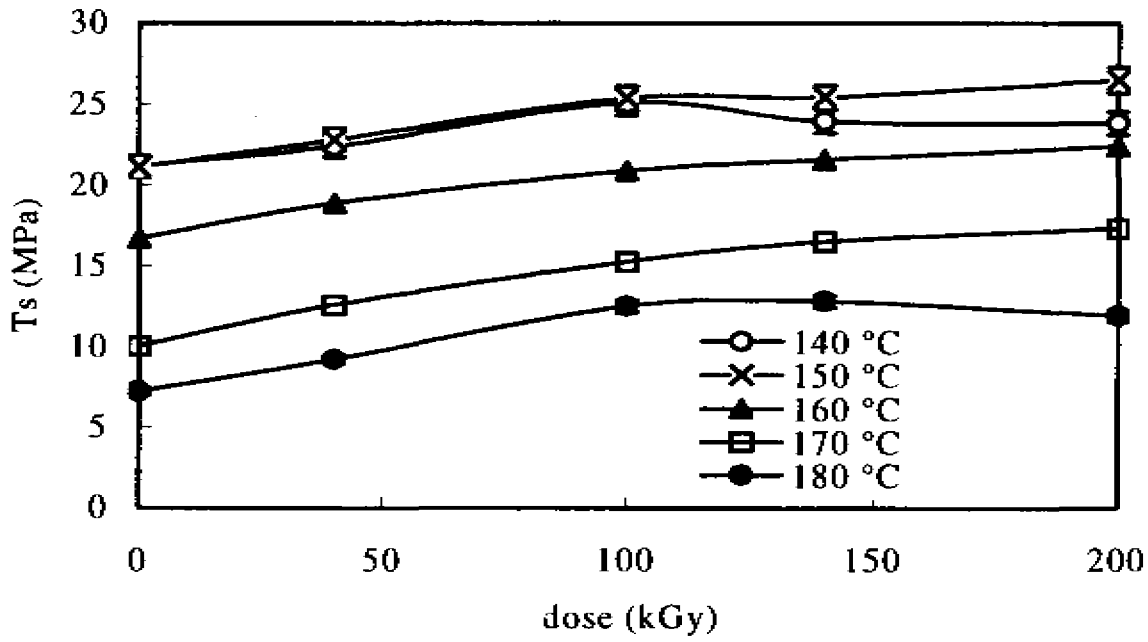

Fig. 2: Effect of irradiation on tensile strength of PVC / ENR blends at various blending temperatures.

increased interactions between the polymers. However at higher doses, the role of irradiation in enhancing interaction between the polymer become less effective as the blends were not homogeneous compared to those prepared at 150°C. The excessive crosslinks formed at above 100 kGy could account for the drop in Ts. The fall in Ts above 100 kGy for blends mixed at 180°C could be associated with irradiation-induced degradation as the blend has readily undergone excessive thermal degradation during blending, implying radiation-induced degradation do occur in the blends.

Modulus

The effect of blending temperature on the M100 of the blend with increasing irradiation dose is illustrated in Fig. 3. The modulus depends directly on crosslink density or perfect network [22]. Thus, the increase is crosslink density reflected from the enhancement in M100 with irradiation dose. The drop in M100 at 100 kGy for blend prepared 180°C is again an indication of radiation-induced degradation. This trend is in perfect agreement with Ts results. Clearly, the M100 further confirms the observation on the Ts results.

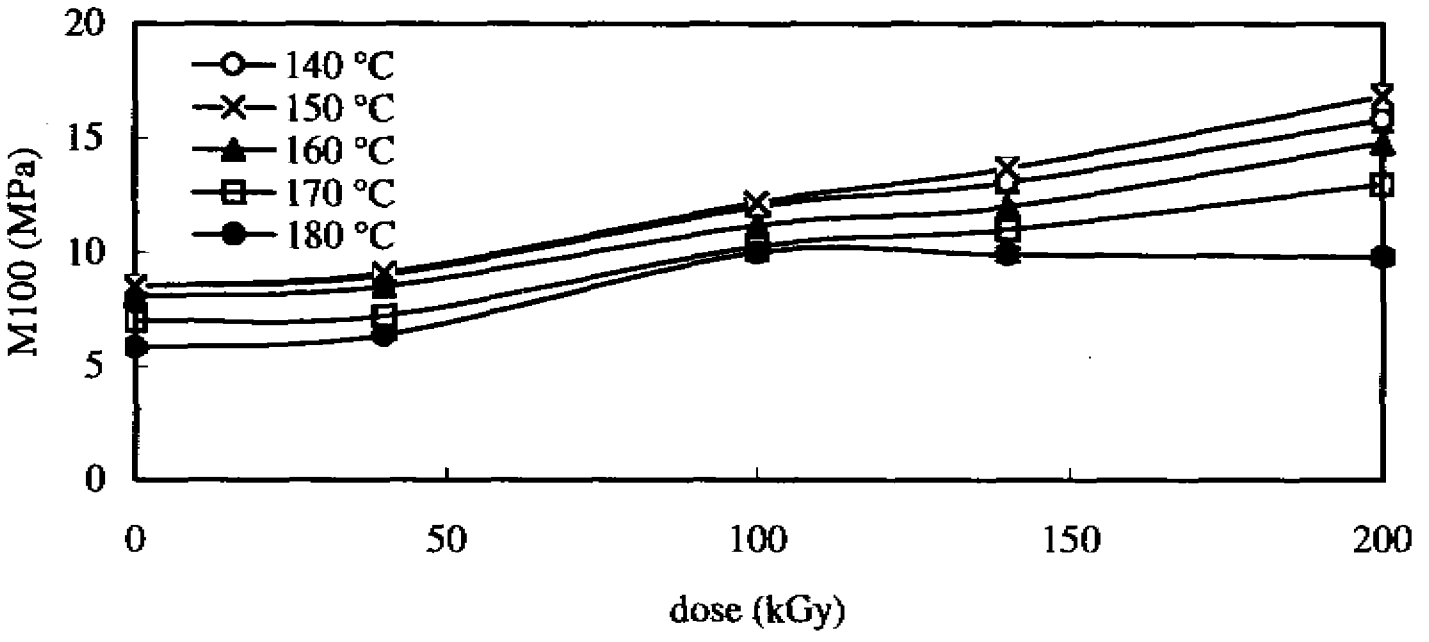

Fig. 3: Effect of irradiation on M100 of PVC / ENR blends at various blending temperatures.

Gel fraction.

Generally, the extent of radiation-induced crosslinking can be estimated from gel fraction determination [23]. Thus, in order to elucidate the effect of blending temperature on radiation-induced crosslinking, the gel fraction of the blends were determined and plotted in Fig. 4.

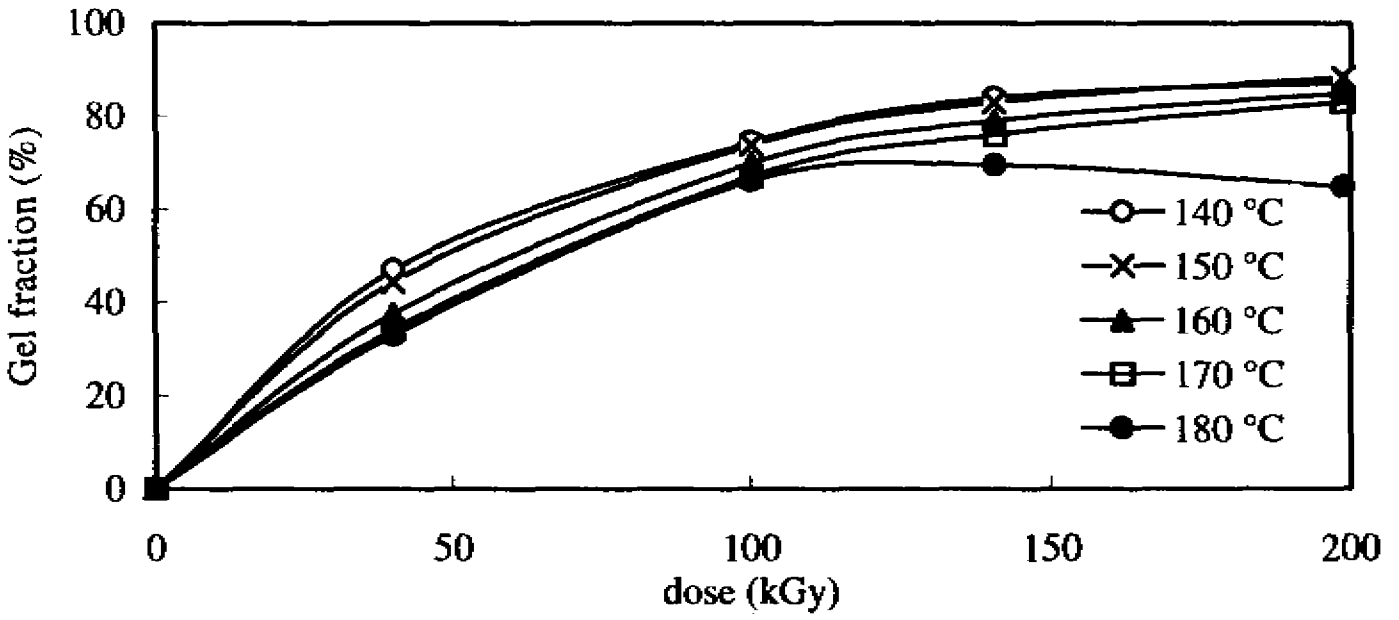

Fig. 4: Effect of Irradiation on gel fraction of PVC / ENR blends at various blending temperatures.

The increase in gel fraction of the blends upon irradiation observed in Fig. 4 is in perfect agreement with our previous findings [5-9]. The lower gel fraction values observed with increasing blending temperature above 150°C confirm that the initial blend stability is crucial in controlling the formation of crosslinks upon irradiation. The decline in gel fraction of blend mixed at 180°C above 100 kGy further supports our notion on occurrence of radiation-induced degradation. Another salient point is, there is no appreciable difference observed between gel fraction of blend obtained at 140°C and 150°C. Their gel faction values found to be the same. This observation agrees well with our assumption that the dissimilarity observed between these blends in Ts at 100 kGy and

above is associated with the better interaction achieved for the blend prepared at 150°C. Further to this, it is expected DMA will provide more definite evidence on radiation- induced interaction in the blends.

Dynamic Mechanical Analysis

For this purpose the blends prepared at 140°C and 150°C mixing temperatures are selected. The presence of a single tan δ peak in DMA results is an indication of a homogeneous single phase or good dispersion [24,25].

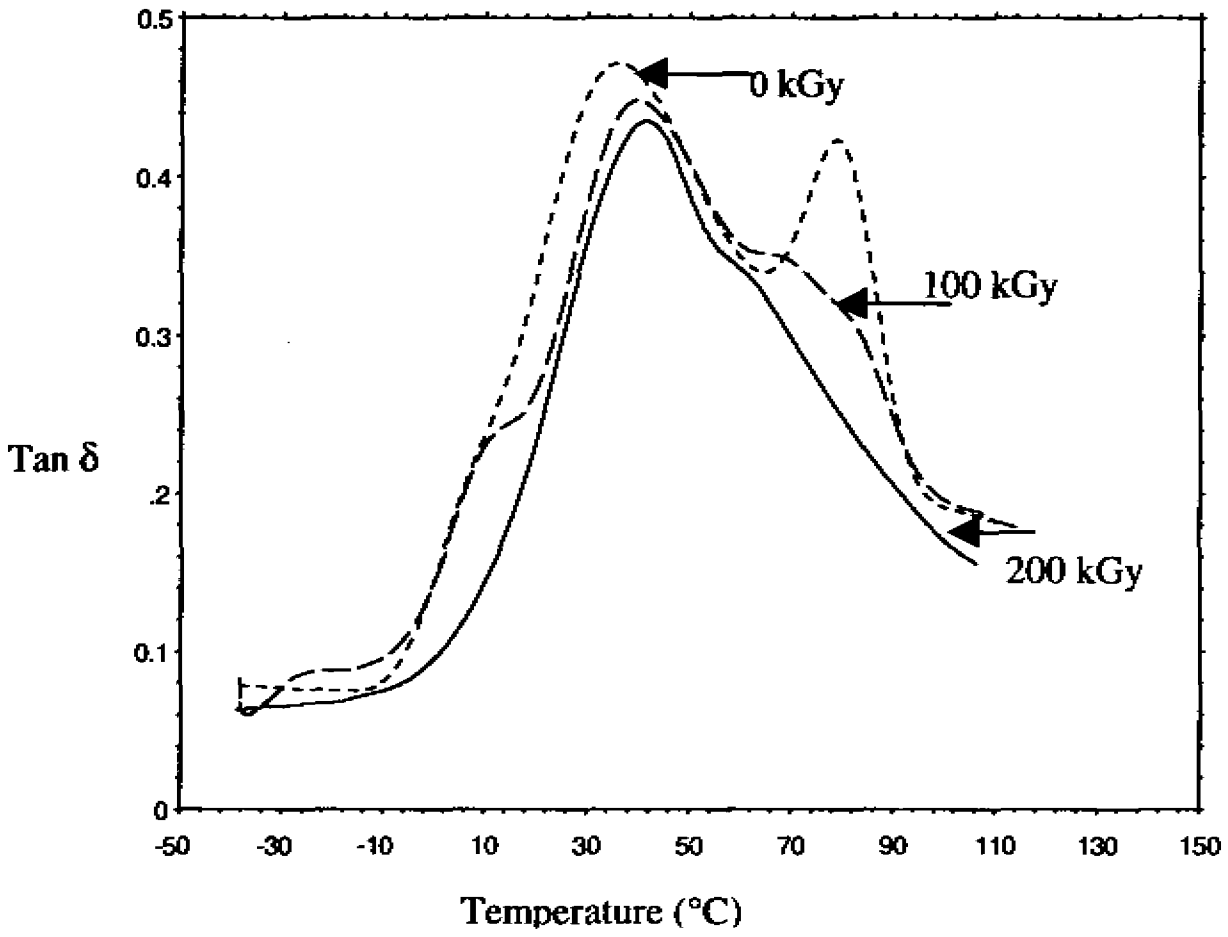

Fig. 5: The effect of irradiation on the temperature dependence of tan δ of PVC/ENR blend prepared at 140°C mixing temperature.

For PVC/ENR blends, numerous findings of a single T_g have been reported, which yield favorable mechanical properties [12,14,26-27]. The changes in tan δ plots with irradiation dose which obtained for the 140°C and 150°C mixing temperatures are illustrated in Figs. 5 and 6 respectively.

Here, the temperature corresponding to tan δ maxima (tan δ_{max}) is taken as glass transition temperature, T_g. From Fig.5, it is obvious that prior to irradiation two peaks are significant for sample blended at 140°C. The temperature of the first peak which is intermediate between T_g of ENR and PVC and a second peak corresponding to T_g of PVC can be noted. The second peak disappears gradually with the increasing irradiation dose. At 100 kGy the tendency towards forming a single peak is observed. The peak corresponding to T_g of PVC found to disappear completely at 200 kGy irradiation dose. Besides that the peak signify the miscible blend (the intermediate peak between T_gs of ENR and PVC) found to shift towards higher temperature as the radiation dose increases. These findings reveal that the radiation-induced reactions in the blends have resulted in increased interactions between ENR and PVC. Although the 140°C mixing temperature was insufficient to produce completely miscible blend, the further interaction in the blend upon irradiation has improved the miscibility of the system..

In order to further support this contention, the tan δ peaks obtained at 0, 100 and 200 kGy irradiation doses for blends prepared at 150°C mixing temperature were compared. Fig. 6 shows a single peak for blend prepared at 150°C. This is in perfect agreement with several reports [12,14,26-27]. It also apparent from Fig. 6 that the tan δ_{max} shift to higher temperature gradually with increasing irradiation dose, implying, that the radiation-induced reactions in the blend had resulted in such shifting. Similar observation also noted in Fig .5 for blends prepared at 140°C.

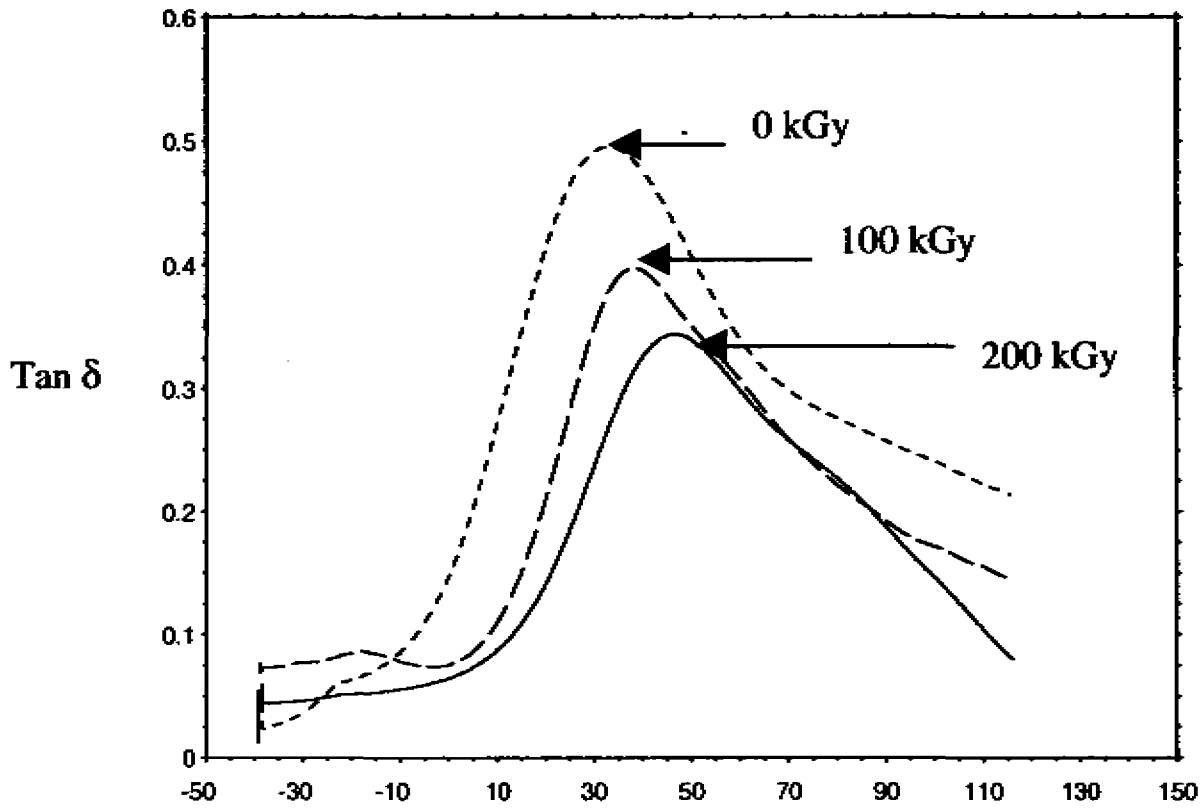

Fig. 6: The effect of irradiation on the temperature dependence of tan δ of PVC/ENR blend prepared at 150°C mixing temperature.

It is also worth noting, that the bases of tan δ curve for the blend mixed at 140°C wider than for the blends mixed at 150°C. Furthermore, these width found to decrease gradually with the increasing irradiation dose for both 140°C and 150°C mixing temperatures. Such observation is believed to be attributed by the reduced heterogeneity in the blend as a consequence of increased interchain chemical interaction upon irradiation. It has been amply demonstrated that the damping curve of dynamic properties of any heterogeneous copolymer reflects the broadening of the transition region due to the increase in heterogeneity [28]. If the molecular interaction between the two types of polymers is high, the effect of interchain chemical heterogeneity is small, so there will be a sharp pear in the transition region [29].

The shifting in T_g and the lowering of the tan δ_{max} magnitude could also associated with the increased crosslink density with irradiation. A number of studies have been made which relate the distance between crosslinks to the shift in T_g, proven that T_g increase with increase in crosslink density [30-34].

CONCLUSIONS

The above discussion clearly illustrates the importance of blending temperatures in ensuring the enhancement of PVC/ENR blend properties through irradiation. Results reveal that under prevailing conditions maximum enhancement in PVC/ENR properties can be achieved by irradiating a miscible PVC/ENR blend system, which obtained at optimum blending temperature. The tan δ curves of irradiated and unirradiated PVC/ENR blend mixed at 140°C indicate that the miscibility of PVC/ENR blends can be achieved through irradiation-induced reactions. The degree of radiation-induced crosslinking found to be less in blends which readily undergone thermal degradation. The occurrence of radiation-induced degradation was prominent at above 100 kGy in blends, which were subjected to excessive degradation. Therefore regardless to the actual radiation-induced reaction involved the importance of blending temperature in maximizing the positive effect of irradiation and the role of irradiation in increasing the miscibility of PVC/ENR blend is apparent.

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