RADIATION EFFECT ON PVC / ENR BLENDS

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Abstract

The effect of irradiation, with dose ranging from 20 to 100 kGy on the physical properties of Polyvinyl chloride / Epoxidised Natural Rubber Blends (PVC / ENR blends) were investigated. The enhancement in tensile strength, elongation at break, hardness, and aging properties of the blends have confirmed the positive effect of irradiation on the blends. While crosslinking of the ENR phase proved to play a major role in the improvement of mechanical properties of blends, it is evident from infrared spectroscopic studies the irradiation - induce interaction between ENR and PVC at a molecular level. The results also revealed that at any blend composition the enhancement in properties depend on the irradiation dose which controls the degree of radiation induced crosslinking. The single glass transition temperature obtained confirms that the blends remain miscible upon irradiation. However, the evidence unveiled the specific nature of interaction involved and the enhancement in the miscibility of the blends by irradiation.

Keywords : PVC / ENR blends, irradiation, crosslink, enhancement, miscibility

INTRODUCTION

Epoxidised natural rubber (ENR) which exhibits a relatively high polarity compared to natural rubber has attracted interest in the field of polymer blending [1-3] . It has been reported that PVC / ENR system has a high level of ply adhesion [4] . Extensive studies on PVC / ENR blends is in progress. Earlier reports [1,5,6] and later work by Zainal et al. [7] indicate the need of using suitable mixing conditions to attain optimum blend properties. Varugese and co-workers [3] as well as Margaritis et al.[2] showed that PVC/ENR blends exhibit a single glass transition temperature,T_g , which lies between that of PVC and ENR , thus asserting compatibility at a molecular level. Margaritis et al.[3] had specially identified the 50 % epoxidation level of olefinic species in natural rubber which known as ENR50 is essentially required in order to attain miscibility with PVC. Findings also indicated that PVC / ENR50 blends were miscible at any blend ratio [3,8] suggesting the diversification in term of processing and properties of PVC/ENR50 composite.

Apparently, most of the findings on PVC / ENR50 blends found to be focus on aspects of miscibility, rheology as well as morphology with regard to mechanical and thermal blending. Until now, no fundamental work have been performed on the effects of irradiation on the PVC / ENR50 blends although high energy irradiation (gamma or electron beam) is a well known technique for the modification of polymers[9]. In fact, attempts have been made to crosslink one of two polymers in a completely miscible blends system. For example, Nishi and Kwei[10] studied on polyvinylmethylether / polystyrene (PVME / PS) 50 / 50 blend and succeeded in raising the low critical solution temperature (LCST) with gamma irradiation via crosslinking of the PVME chains.

This paper will present some interesting findings on the effects of electron beam irradiation on PVC/ENR50 blends in relation to enhancement in the mechanical properties of the blends.

EXPERIMENTAL

Material and Formulations.

Epoxidised Natural Rubber, grade "ENR 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., Ca / Zn - based stabilizer " Baerostab NTMZ-5 " was kindly

donated by Baerlocher Far East Pte Ltd., Singapore; Di octyl phthalate (DOP), used with the Ca / Zn stabilizer, was purchased from Aldrich Chemical Company, Inc. The full recipes of the blends are given in Table I.

Table I. Formulations of PVC / ENR50 blends

Materials	Blends					
PVC (phr)	0	30	50	70	80	100
ENR50 (phr)	100	70	50	30	20	0
Ca/Zn (phr PVC)	-	2	2	2	2	2
DOP (phr PVC)	-	5	5	5	5	5

Blends preparation

PVC, DOP, and stabilizer were premixed at room temperature with a Table Top high speed mixer at 1200 rpm for 10 minutes. Melt blending was carried out at 160°C at 50 rpm rotor speed with a Brabender Plasticorder Model PL 2000 having equipped with a kneader-chamber (W50E) and mixing cam attachment. The blending was done as follows:

When the desired temperature was reached, ENR was charged into the mixing chamber and was mixed for 1 min. The PVC compound was then added, and the blending was continued for a further 4 minutes.

The blends obtained from the Brabender Plasticorder were then compression molded into 1 mm thick sheets under a pressure of 150 $kgcm^{-2}$ at 160^0C for 3 minutes. The sheets were than immediately cooled between two plates of cold press at 25^0C. Dumbbell shaped test pieces were cut from these sheets in accordance with ASTM D1822 - L.

Irradiation

The molded sheets and dumbbell test pieces were irradiated in air using a 3 MeV electron beam accelerator at doses of 20,40,60,80 and 100 kGy. The acceleration energy, beam current and dose rate utilized were 2 MeV, 2 mA and 20 kGy / pass respectively.

Measurement of mechanical properties

The tensile strength was measured on a Toyoseiki Universal testing machine (model Strograph-RI) with a crosshead speed of 50 mm / min. Altogether eight samples were used for tensile and elongation at break test and an average of at least six data was taken as the resultant value. While for aging, samples were aged in an oven at 70^0C for 7 days before testing. The Rockwell R hardness test was carried out according to ASTM D785 using HA-101 Rockwell Automatic Digital Hardness Tester.

Gel fraction

The gel fraction was determined by extraction in tetrahydrofuran, THF at 50 ± 2°C. The blends were solvent extracted using THF for 48 hours and the extracted samples were dried and weighed until a consistent weight was obtained.

Infra red spectra (IR)

The Fourier transform infrared spectroscopy, FTIR, spectra were obtained with a Perkin-Elmer 843 spectrophotometer by the Attenuated Total Reflectance (ATR) technique for 50/50 PVC/ENR blend irradiated at 80kGy dose. The difference in spectra due to irradiation was recorded using a un - irradiated blend as reference.

Glass Transition Temperature, Tg

In order to determine the glass transition temperature, Tg, a Dynamic Mechanical Analysis was performed using a Free Torsion Damping Type Rheometer RD - 1100AD (Rhesca Co. Ltd., Japan) at frequencies between 0.2 and 1 Hz. The measurements were carried out at a heating rate of 2°C / min over a temperature range of -100°C to 150°C.

Gel fraction

Generally, the extent of radiation induced crosslinking of polymers can be estimated from gel fraction determination [11]. Thus, in order to elucidate the radiation induced crosslinking, the gel fraction of the blends was determined and the results were plotted in Fig. 1. Apparently, the stabilized PVC did not render any values for gel fraction, while the increase in gel fraction with irradiation dose for blends was observed to be enhanced by increasing the ENR50 content with the highest gel fraction for the pure ENR50 at all irradiation doses. This trend could be attributed to the ability of ENR50 to crosslink upon irradiation . On the other hand, the results obtained here also suggests that under the irradiation conditions employed, crosslinking was not induced in PVC. This observation is in general agreement with numerous reports on the radiation effects on PVC [11,12,13].

Tensile strength

The details of the mechanical properties of un - irradiated PVC / ENR50 blend system have been published [1,5,14] and only discussions with special focus on effect of irradiation on blend properties will be provided here. Figure 2. illustrates the tensile strength, Ts, as a function of irradiation dose. It is obvious that upon irradiation enhancement in Ts occurs for the pure ENR50 and the blends while, as expected, the Ts of PVC is not affected . This behaviour is believed to be due to the formation of radiation - induced crosslinking in the ENR phase as evidenced from the gel fraction values. However, it is worth noting that the pure ENR50 shows only slight enhancement in tensile strength with increasing irradiation dose relative to the improvement observed for the blends. Moreover, although irradiation had remarkable influence on the gel fraction of the pure ENR50, the improvement in Ts is found to be only marginal. This indicates that the increase in Ts of the blends could also be due to the radiation - induced chemical interaction between the polymers.

A similar observation was reported by Birkinshaw and Buggy [15] in their work on irradiated high impact polystyrene modified polybutadiene type. They reported that the effects of gamma irradiation on the mechanical properties of high impact polystyrene are much greater than those observed in the homopolymer and they have associated this behaviour with radiation - induced crosslinking of

polybutadiene as well as the modification at a molecular level between the component polymers which offered by irradiation at the interface.

Elongation at break

Plots of the elongation at break, Eb, vs. irradiation dose for the blends are shown in Fig. 3 . Generally increasing the irradiation dose causes a substantial reduction in the elongation at break of the blends. Such a decline is expected since in general, the mechanical property which is most sensitive to radiation degradation is the Eb and this property is found to invariably decrease regardless of whether chain scission or crosslinking is predominant[16] .

Therefore, the reduction in elongation at break could be attributed to the reduced segmental mobility of the blends which resulted from the increased crosslinking of the ENR phase. In other words, the onset of crosslinking reduces the ability of the rubber chain to plastically deform hence a progressive reduction in Eb with increasing dose is noted. On contrary, the radiation induced degradation which may have occurred in either polymers in the blends could also account for the fall in Eb with dose.

However, looking at the plot for pure ENR, the trend is not the same. Here, the initial decline in elongation at break at 20 kGy is a clear evidence of radiation - induced degradation . The rise in elongation at break from 20 to 60 kGy could be associated with the formation of radiation - induced crosslinks coupled with the ability of the rubber to undergo strain - induced crystallization. This is similar to the sulfur vulcanized ENR50 which was found to be capable of undergoing strain - induced crystallization as above[17] . On the contrary, the opposite situation which is observed at doses above 60 kGy explains the further crosslinking of the ENR50 could have introduced irregularity to the rubber chain, thus eliminating the strain - induced crystallization.

Whereas for stabilized PVC, the changes in elongation at break is rather insignificant which is in agreement with the previous results on tensile strength and gel fraction. Hence this points out the fact that beside the crosslinking of the ENR phase, the possibility of interaction between the two polymers with irradiation must also be considered in overall enhancement of the blend properties. In line with this several reports [18-20] further suggests that the epoxy groups in ENR could possibly interact with other polymers to form crosslinks. To add to this, findings by Liu et al.[21] in their work on "Enhanced interfacial radiation - induced reaction for improving the interfacial adhesion of incompatible polypropylene / cis 1,4

polybutadiene blends" have confirmed the improved interfacial adhesion between dispersed phase and matrix achieved by radiation - induced crosslinking and grafting between the polymers at the interfacial region.

Hardness

The composition dependence of the hardness of the sample with increasing irradiation dose is illustrated in Fig. 4. In agreement with the results on tensile strength, elongation at break, and gel fraction, the hardness of stabilized PVC was also not influenced by irradiation dose. ENR50 shows a remarkable increase in hardness with irradiation whereas a gradual increase in hardness with dose was observed for the blends. Thus, it is evident that the enhancement in hardness of the pure ENR50 is due to the formation of crosslinks by irradiation as confirmed by gel fraction. In definition, hardness is generally referred to the resistance of a material to local deformation [22], and the results proved that ENR50 show more pronounced increase in hardness with increasing dose compared to the tensile strength values. Importantly, it is clear that radiation - induced changes which have particular effect on the ability of the rubber to crosslink can be expected to influence the mechanisms of reinforcement. It is also probable that crosslinking in the rubber phase has proceeded to such an extent that only minor energy dissipation occurred during extension under stress as evidenced from results on tensile strength vs. irradiation dose of the pure ENR in this work. This eliminates the possibility of the property enhancement of the blends which occur upon irradiation without the presence of interaction between the constituent polymers.

IR spectra

It has been reported that epoxy resin can crosslink PVC [23]. With reference to the IR spectra obtained for 50% PVC blend (PVC / ENR blend at 50 / 50 ratio), Ramesh and De[24] have confirmed that ENR and PVC can react together through the allylic chlorine sites of PVC and the epoxy moieties in ENR to form ether crosslinks. They found a reduction in epoxy ring peak at 875 cm^{-1} and an increase in ether peak intensity at 1072 cm^{-1} as thermal effect. Here, an almost similar observation was noted on the IR spectrum shown in Fig. 5 for 50% PVC blends irradiated at 80 kGy, thereby confirming similar reaction as reported by Ramesh and De[24] has occured upon irradiation of the blend. Thus, it is evident that, irradiation enhances interaction between ENR50 and PVC.

The kinetics of the light - induced crosslinking of epoxidized liquid natural rubber was studied by Decker et al [25] . Their report proves that the ring opening of the epoxy group upon UV irradiation leads to crosslinking in the rubber. In addition, upon exposure to irradiation PVC degrades by elimination of HCl[12,26] . It is believed that the HCl generated could also catalyze the ring opening reaction of the epoxide group leading to the formation of crosslinks via ether groups[7, 27] .

Further evidence shows that there is a significant reduction in the absorption peaks of the isoprene unit (C=C cis) at 837 cm^{-1} and 738 cm^{-1} [28] in the IR spectra (Fig.5). This consumption in double bond following irradiation is also related to crosslink formation in the rubber phase [29,30]. Besides this, another possible radiation - induced reaction is the formation of grafted copolymer of PVC onto the crosslinked ENR50 network . In view of this, Gisbergen and Overberg[31] have confirmed that the improvement in the elastic behaviour of the EPDM / PP blend with irradiation is due to grafted copolymer of PP onto the crosslinked EPDM network. This implies that upon irradiation, the PVC / ENR 50 blend network structure might consist of crosslinked ENR along with the copolymer of PVC, crosslinked PVC / ENR50 and furanized ENR50. However, it is important to mention here that this evidence unveiled the exact nature of specific interactions involved between the two different polymers upon irradiation.

Aging properties

The aging properties of the un - irradiated PVC / ENR50 blends and the blends which were irradiated at 80 kGy, indicated by the retention of tensile strength after being aged at 70°C in air for 7 days, is presented in Fig. 6. Apparently, the irradiated blends depict improved retention in tensile strength compared to the un - irradiated ones. This is believed to be due to crosslinking of the rubber phase coupled with the enhanced compatibility of the blends obtained on irradiation as a result of interaction at a molecular level which supported by IR studies.

Interestingly, looking at 0 to 50% PVC blends, the composition dependence of retention in tensile strength exhibits opposite trend relative to the unirradiated ones. This trend most probably indicates the positive effect of crosslinking of the ENR phase upon irradiation. Hence, the retention in Ts decreases with a reduction in ENR content in the irradiated blends. Apparently, for blends with less than 50% PVC, the dominating phase is the ENR50, implying that the blend properties are governed by the ENR.

At 50% PVC content, a phase inversion could have taken place where the PVC and ENR50 show tendencies to become a continuous phase [5]. Accordingly, the increase in % retention from 50 to 70 % PVC could be due to the increased chemical interaction by irradiation with increasing PVC concentration which ensures availability of more allylic chlorine site. On the other hand, the decline in % retention above 70 % PVC could be associated with the insufficiency of ENR to provide epoxy sites to react with the PVC which resulted in decreasing compatibility between the polymers. This behaviour is again proof of increased interaction between the PVC and ENR50 chains upon irradiation. The explanation on phase inversion also coincides with the changeover from property additivity to synergistic behaviour [32].

For un - irradiated samples the enhancement in aging properties with increasing PVC content is believed to be attributed by the protection given by the PVC phase, akin to those reported by George et. al. [33] in which the presence of PVC enhances the thermal aging of NBR in PVC / NBR blends. Thus, on comparing the explanation for irradiated and un - rradiated blends, a much clearer picture on how irradiation accounts for the improvement in aging properties of blends could emerge.

Glass Transition Temperature,T_g

The T_g values for un - irradiated samples and samples irradiated at 80kGy which were obtained from Dynamic Mechanical measurements are reported in Table II. For comparison purposes, only the 30%, 50% and 70% PVC blends along with the pure PVC and ENR were chosen for T_g measurements.

Table II. T_g values of the blends and the respective homopolymers before and after irradiation.

	T_g (°C)	
Sample	OkGy	80kGy
ENR50	-7	5
30%PVC	10.5	14
50%PVC	33	38.5
70%PVC	49.5	53
PVC	79.5	78

Here, the T_g values were taken as the temperatures that correspond to the loss tangent peak since they coincide with T_g values determined by other methods, for example, free volume studies [34] . In this attempt, the effect of irradiation on the T'_g s of the blends were compared with both homopolymers, PVC and ENR. Interestingly, a shift of T_g towards higher values with irradiation is observed for blends as well as for the homopolymer ENR. On the contrary, a slight drop in T_g is noted for irradiated PVC compared to the un - irradiated one. This clearly implies that the increase in T'_g s of the blends on irradiation could be attributed to the radiation - induced crosslinking of the ENR phase. Again this findings correlate well with the results on gel fraction. On the other hand, radiation - induced degradation by liberation of HCl [12,25] may account for the drop in the T_g of PVC. Interestingly results show that at the range of dose employed, the degradation of PVC did not show considerable influence on the mechanical properties of the PVC which is in perfect agreement with the report by Landfield[35]. Subsequently, this observation reaffirms the important role played by ENR in improving the physical properties of the blends under prevailing irradiation conditions.

Another salient point is a single Tg, intermediate between that of irradiated PVC and ENR, noted for the irradiated blends. This conforms with what is generally expected for any miscible polymer - polymer system [36,37]. Furthermore this findings is in accordance with those reported by several researchers [3,8,14] working with miscibility of un - irradiated PVC / ENR50 blends. Consequently, it is evident that the irradiated PVC / ENR50 blends are also miscible, presumably, irradiation enhances the miscibility. With regard to the blend miscibility, further evidence is needed in order to prove that irradiation improve the miscibility of the PVC/ENR50 blends.

CONCLUSIONS

The effects of EB irradiation on the mechanical properties of PVC / ENR50 blends are found to be greater than that observed in individual polymers. Studies also reveal that this improvement in properties is not a simple function of crosslinking of the ENR50 phase. Another factor which could contribute towards the enhancement is believed to be the increased interaction between the two different polymers involved which lead to the improved miscibility of the blends. However, the irradiation degradation of PVC which were noted has to be taken into account in order to maximize the positive effect of irradiation on PVC / ENR50 blends before embarking on a specific blend recipe in relation to application.

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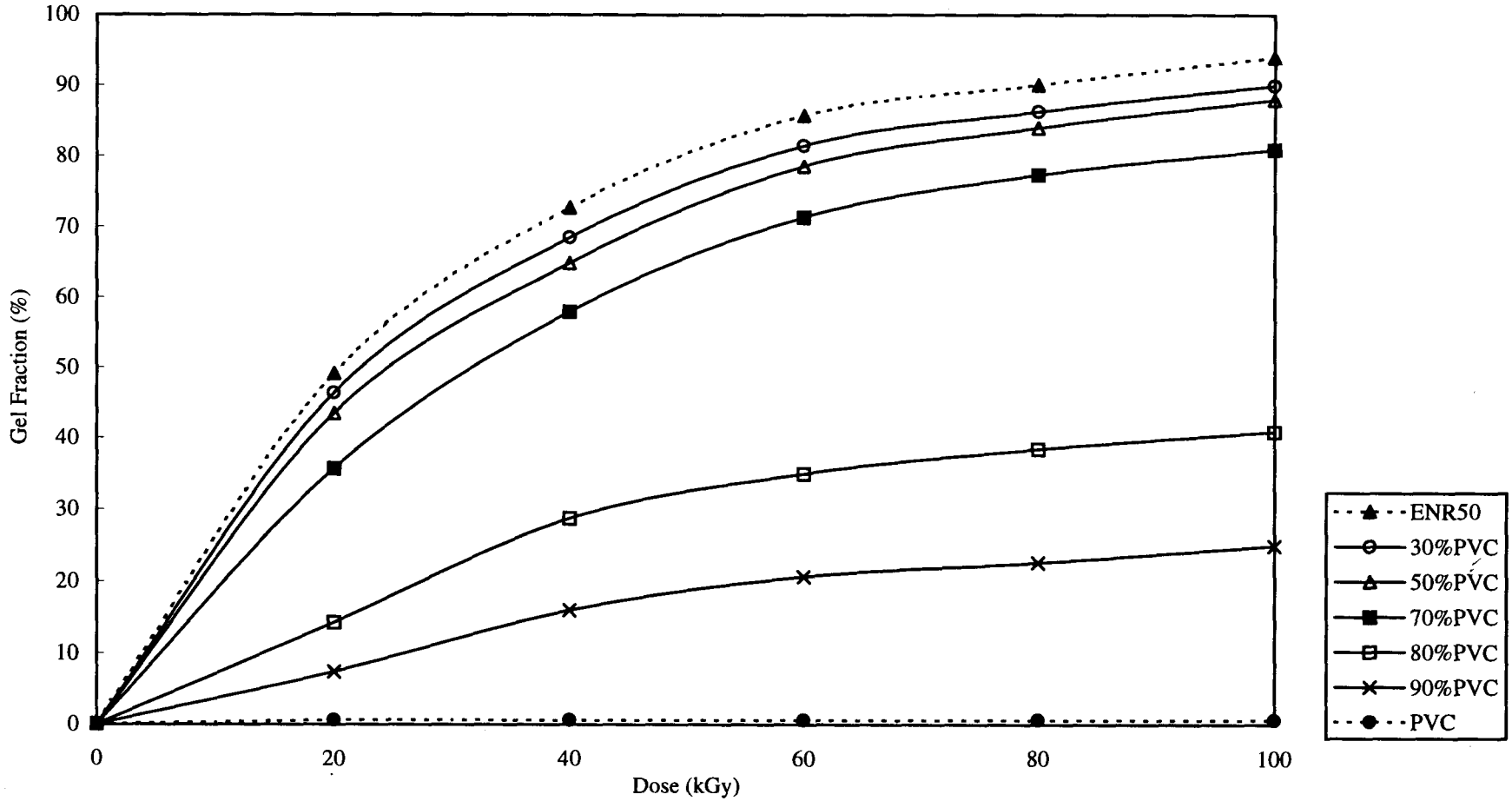

Figure 1. Effect of irradiation on gel fraction of PVC/ENR blends.

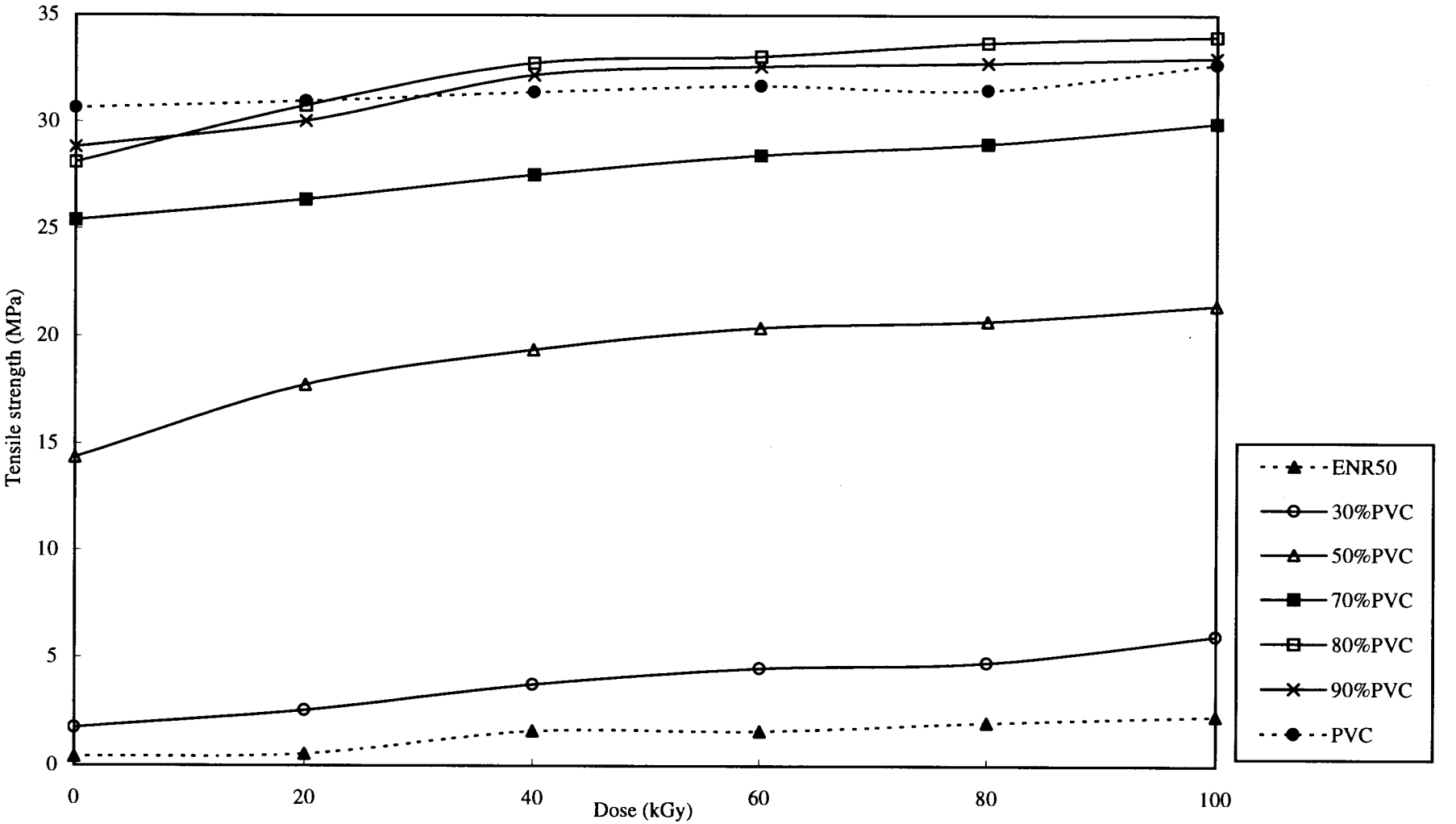

Figure 2. Effect of irradiation on tensile strength of PVC/ENR blends.

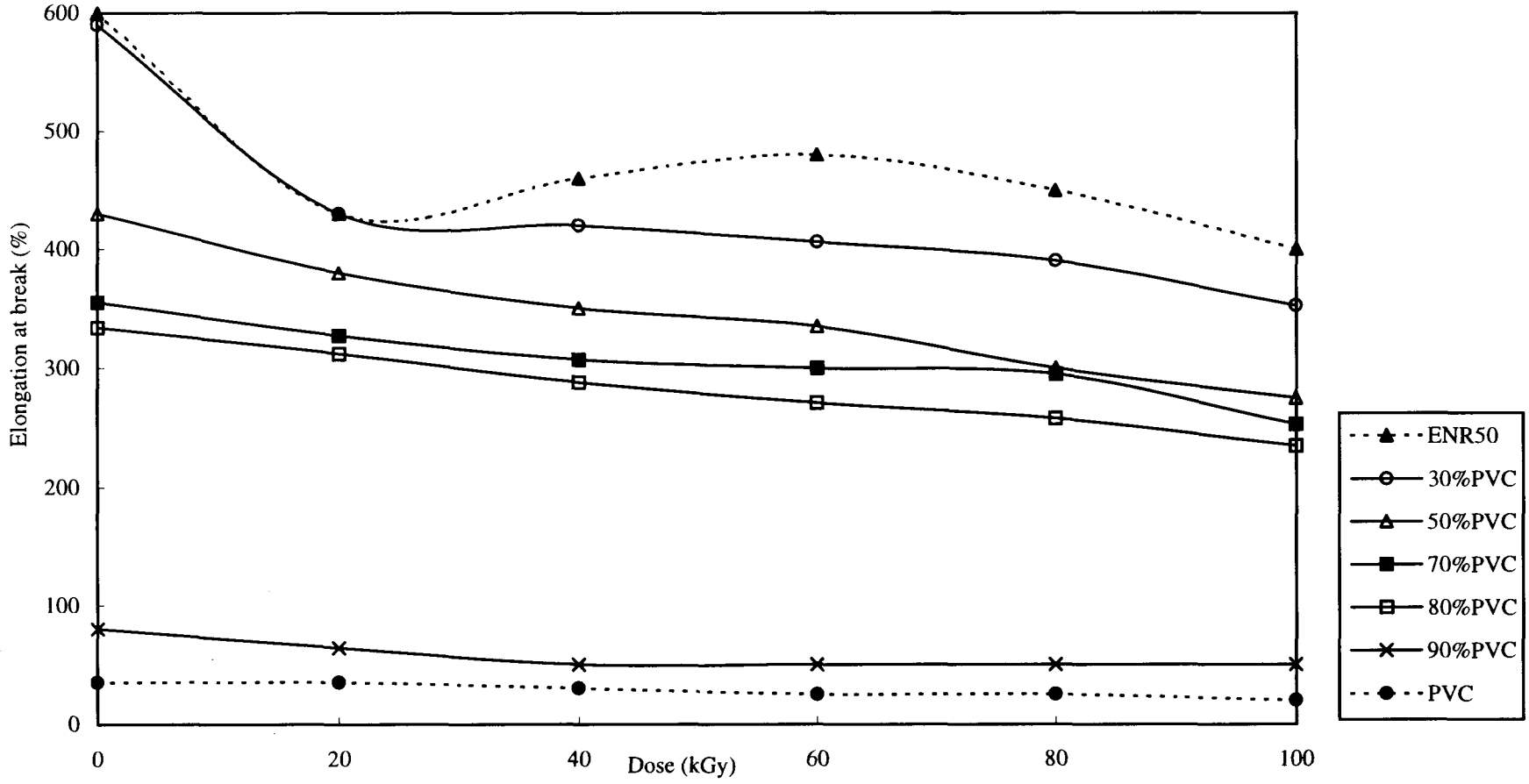

Figure 3. Effect of irradiation on elongation at break of PVC/ENR blends.

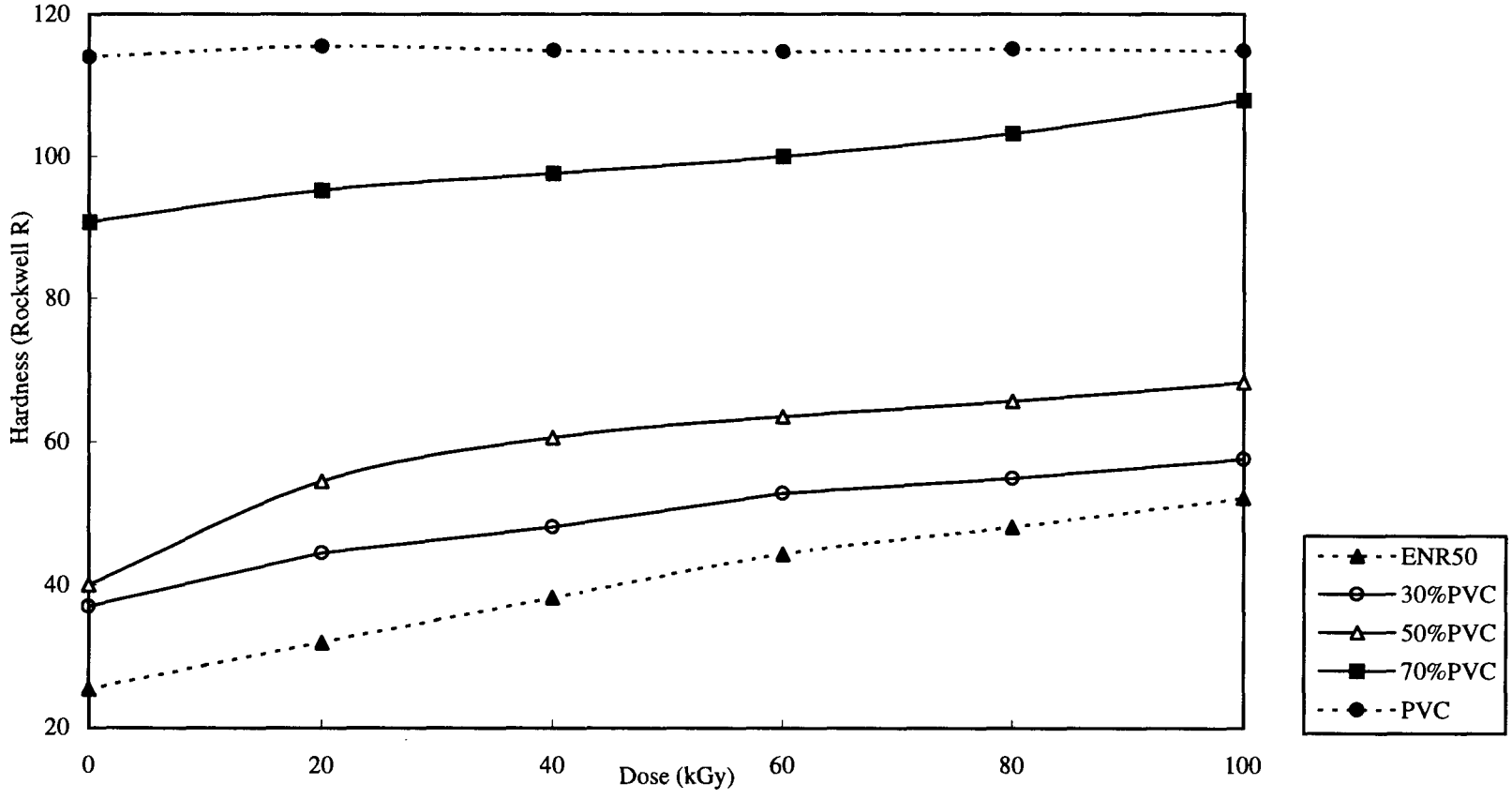

Figure 4. Effect of irradiation on hardness of PVC/ENR blends.

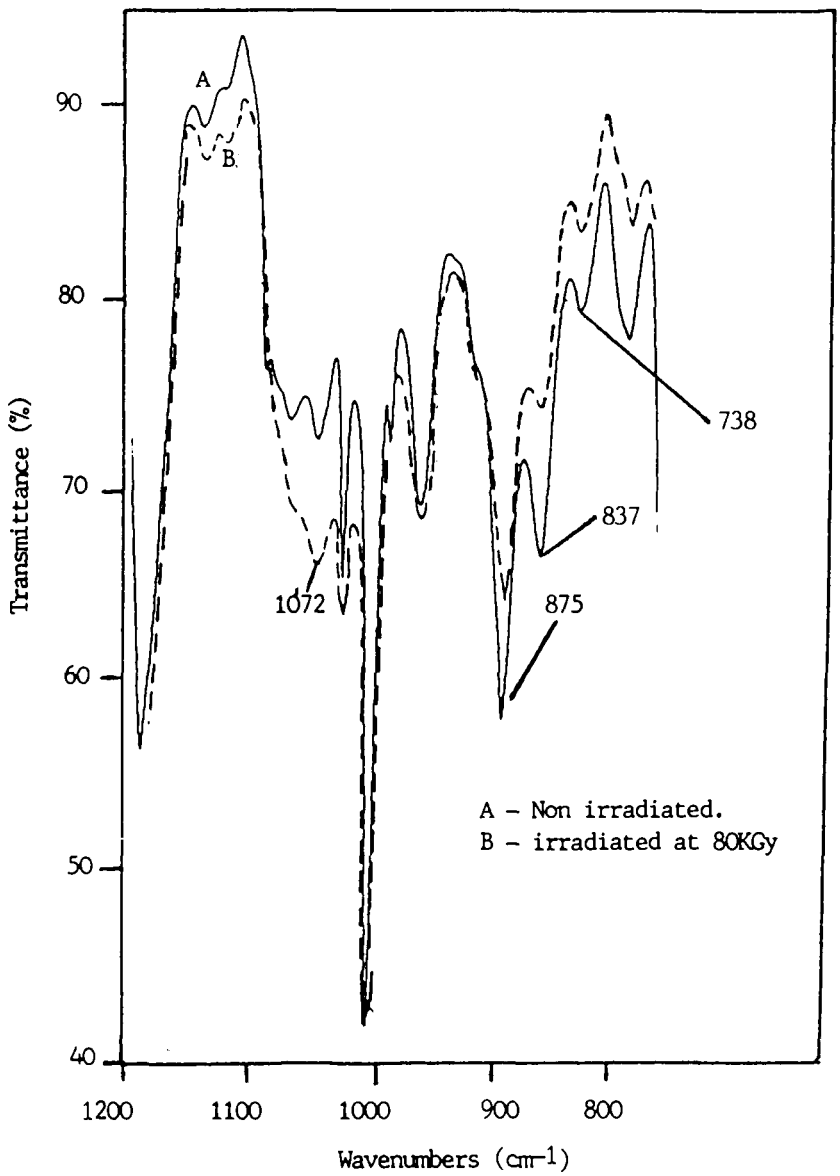

Figure 5. IR Spectra of 50% PVC blend

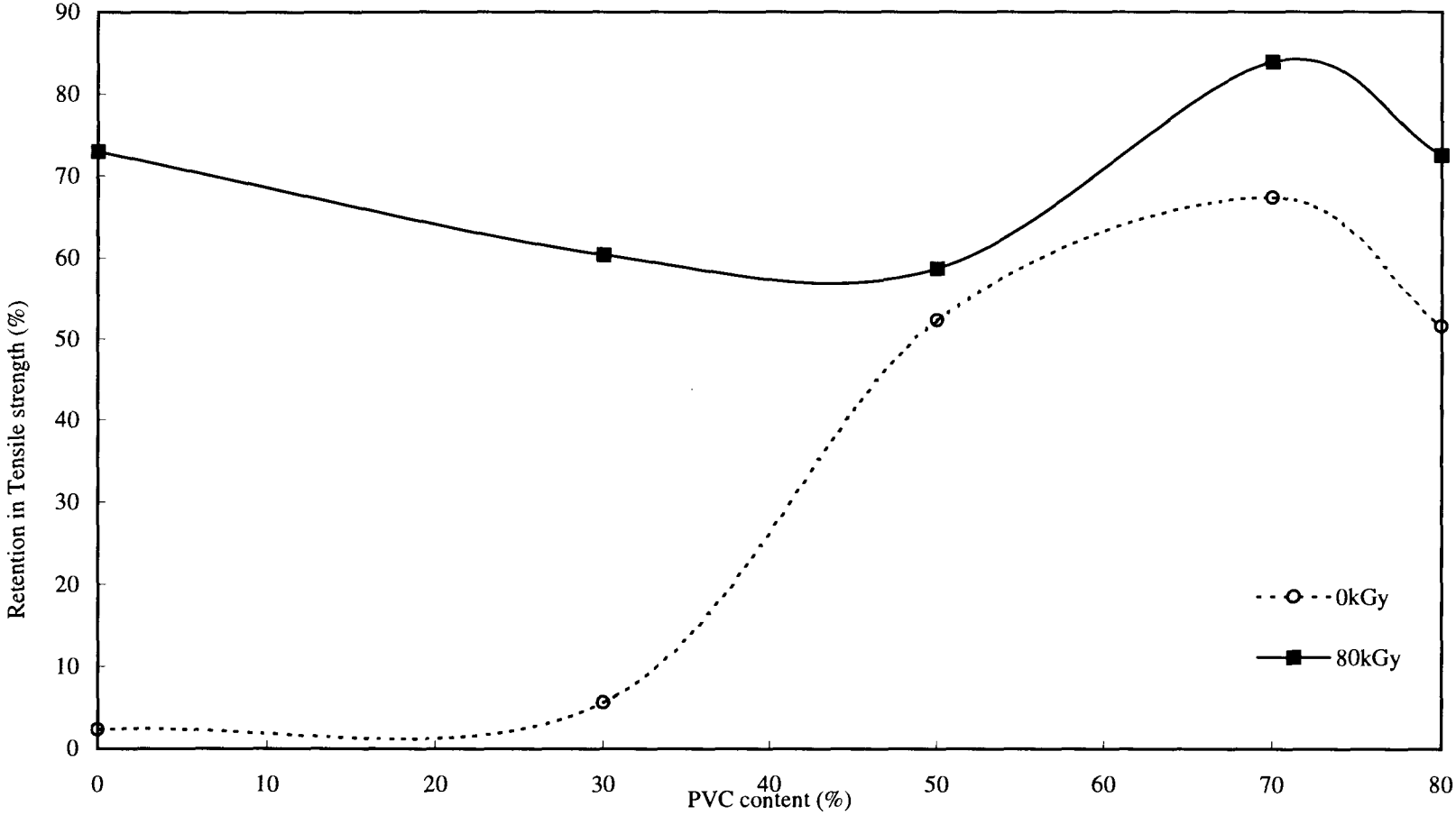

Figure 6. Retention in Ts of PVC/ENR blends after aging at 70C for 7days.