

Dynamic Mechanical Analysis of Polyethylene and Ethylene Vinylacetate Copolymer Blends Irradiated by Electron Beam

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ABSTRACT: Dynamic mechanical properties of nonirradiated and irradiated blends of polyethylene (PE) and ethylene vinylacetate (EVA) copolymer have been determined. Effect of addition of EVA and radiational crosslinking on loss and storage modulus, $\tan \delta$, and transition temperatures were determined. Increase in transition temperatures on exposure to radiation and decrease in transition temperatures with addition

of EVA is observed. Peak broadening is observed on exposure to radiation. Values of the storage modulus increase while that of loss modulus and $\tan \delta$ decrease on crosslinking. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2429–2434, 2002

Key words: crosslinking; dynamic mechanical analysis; electron beam irradiation; ethylene vinylacetate; polyethylene

INTRODUCTION

Molecular mobility in amorphous or crystalline structures can be stimulated by systematic variation of the applied dynamic mechanical excitation and by temperature variation. Variable parameters are temperature, frequency, and the amplitude for dynamic and static loads. These values can be selected independently from each other and can be held constant. The study of the dynamic parameters over a wide range of temperatures and frequencies provides an insight into the structure of polymers, including correlating impact stability and damping, measuring glass transition temperatures and secondary transition temperatures and their ranges, determining compatibility of blends and degree of miscibility, understanding and optimizing the curing phenomenon in rubber, correlating acoustic or vibration dissipation with damping.

According to the literature,¹ dynamic mechanical analysis of polyethylene prior to melting reveals three peaks termed as α , β , and γ transitions. All these peak transitions correspond to different motions in polyethylene chains. The γ transition occurs in the range of -150 to -120°C . Several controversies still exist about the origin of the γ transition. Illers^{2,3} has proved that the γ peak is due to the amorphous fraction and is absent in 100% crystalline polyethylene, while Sinnott⁴ and Hoffman et al.⁵ proposed that it is strictly

due to defects in the crystalline phase. Various other mechanisms have been proposed for the γ relaxation observed in melt crystallized polyethylene. The original suggestion^{6,7} of the dynamic mechanical properties of polyethylene was that this relaxation is due to motion of the polymer chains in the amorphous regions. This suggestion was subsequently refined to the motion in the amorphous regions of segments of the chains comprising of three or four CH_2 units.⁸ Further, it was proposed that this motion involves rotation about collinear bonds.⁹ Gray and McCrum¹⁰ concluded that the origin was largely amorphous but then there was a crystalline contribution as well.

Sinnott¹¹ suggested that the γ relaxation in melt crystallized polyethylene is due to the same mechanism as that in the single crystals of polyethylene and crystals of *n*-alkanes, and the γ relaxation in melt crystallized polyethylene does not arise from a discrete amorphous phase, but could originate within a lamellar structure, while Khanna et al.¹² suggested that the γ relaxation involves the motion of a short segment of amorphous polyethylene in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions.

The β relaxation occurs between -30 and $+10^\circ\text{C}$ depending upon the type of polyethylene. The β transition is attributed to the amorphous phase,⁵ which is further confirmed by the fact that single crystals (i.e., no discrete amorphous phase) of linear polyethylene do not exhibit a β relaxation whereas a very small β peak has been reported in bulk polyethylene containing amorphous phase.^{4,5,13} It is generally described that the β transition is due to the motion of branches in the amorphous matrix.^{13–15} It has also been shown that

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TABLE I
Various Compositions Prepared for the Present Study

S. no.	Composition				
	code	LDPE	EVA	Antioxidant	Lubricant
1	C1	100	10	1	1
2	C2	100	20	1	1
3	C3	100	30	1	1
4	C4	100	40	1	1

β relaxation is the glass transition, and influence of physicochemical parameters on the β relaxation can be explained in terms of T_g .¹²

The α transition is usually found between 30 and 120°C depending on the type of polyethylene. It is generally agreed that the α transition is representative of the crystalline phase and originates from some type of motion within crystals.^{14,16,17} It is now well documented^{5,18} that during the α transition the chains within the crystal interiors are mobilized.

It has been shown previously that internal friction of polyethylene, in which the average every 50th carbon atom was crosslinked by radiation with γ -rays from Co-60, was similar over the low temperature region to that of the nonirradiated material.¹³ It has also been shown that the effect of crosslinking on the dynamic properties of the vulcanized rubber is evident above α .¹⁹ Keeping this in view, only α and β transitions are studied in the present work. Dynamic mechanical analyses were carried out at a fixed frequency of 1 Hz and heating rate of 5°C/min from -120 to +120°C. Two transitions, one at -10 to 0°C and the other between 40 and 90°C, which are designated as α and β transitions respectively, were observed.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) grade 22FA002 from Indian Petrochemicals Corporation Limited, and ethylene vinylacetate copolymer (EVA) grade 1802 with 18% vinylacetate content from M/s Polyolefins India Ltd., have been used for the present study. Along with major blending constituents a phenolic antioxidant and a lubricant have also been used.

Sample preparation

LDPE and EVA copolymer in varying ratios along with other formulatory ingredients were melt mixed in an internal mixer of Rheocord RC90 at 190°C for 8 min. The blend compositions used in the present study are depicted in Table I. The blends prepared were compression molded into sheets at 170°C. Sheets were then irradiated by a 2 MeV electron beam accelerator for a total dose of 125 kGy.

DSC analyses

Crystallinity of nonirradiated and irradiated blends were determined by differential scanning calorimeter (DSC), model TA instrument's MDSC-2910. Samples were heated at 10°C/min ramp to erase any shear and thermal history. The samples and reference were then cooled at 10°C/min to room temperature to enable crystallization and then reheated at the same ramp to 150°C. All the measurements were carried out under nitrogen atmosphere.

DMA analyses

Viscoelastic properties were determined using a Du Pont Instruments' Dynamic Mechanical Analyzer model DMA-983. Rectangular bar specimens of dimension 50 × 10 × 3 mm were used for the study. The samples were mounted on vertical serrated clamps installed inside an oven on the instrument. Samples were clamped between the ends of the parallel arms, which are mounted on low force flexure pivots allowing motion in only the horizontal plane. An electromagnetic motor attached to one arm of the clamps drives the arm/sample system to the preset strain (amplitude). As the arm/sample system was displaced, the sample undergoes a flexural deformation. A linear variable differential transformer (LVDT) mounted on one arm measures the sample response to the applied stress.

The sample length between clamp was measured and radiant shield was placed above the sample. The oven was then slide over the sample and screwed into position. A temperature of -120°C was obtained by purging the oven with liquid nitrogen supplied through an LNCA-II tank. Measurements were obtained at a fixed frequency of 1.0 Hz and at a heating rate of 5°C/min. The samples were scanned for their viscoelastic responses including, storage moduli (E'); loss moduli (E''), and internal friction ($\tan \delta$). The test was carried out for nonirradiated control and irradiated samples.

RESULTS AND DISCUSSION

β transition

The β transition peak temperatures (T_g), i.e., the temperature at which maxima in loss moduli occurs, for the nonirradiated control samples are reported in Table II. A decrease in β transition temperature with increase in EVA loading ratios is observed for all the compositions. For the irradiated systems, the peak temperatures are presented in Table III. As observed, the β transition peak temperature increases on exposure to radiation.

TABLE II
Storage Modulus, Loss Modulus, and Internal Friction Values for Non irradiated Control Systems

Composition	Log storage modulus (E) (Pa)			Log loss modulus (E ^l) (Pa)			Internal friction (Tan δ)			Transition temperatures (°C)		
	Low temp. zone, 100°C	Room temp. zone 25°C	High temp. zone, 75°C	γ Transition, zone value	β Transition, peak value	α Transition, peak value	Low temp. zone, -100°C	Room temp. zone, 25°C	High temp. zone, 75°C	β Transition	α Transition	
												β Transition, peak value
C1	9.54	8.76	8.04	7.81	8.11	7.52	0.015	0.110	0.289	50.26	-6.784	
C2	9.54	8.76	8.00	7.81	8.14	7.67	0.016	0.116	0.294	47.82	-7.476	
C3	9.54	8.75	7.96	7.80	8.18	7.73	0.015	0.125	0.298	43.65	-8.726	
C4	9.54	8.76	7.87	7.80	8.20	7.84	0.016	0.130	0.300	41.10	-9.723	

TABLE III
Storage Modulus, Loss Modulus, and Internal Friction Values for Irradiated Systems

Composition	Log storage modulus (E') (Pa)			Log loss modulus (E'') (Pa)			Internal friction (Tan δ)			Transition temperatures (°C)		
	Low temp. zone, -100°C	Room temp. zone, 25°C	High temp. zone, 75°C	γ Transition, zone value	β Transition, peak value	α Transition, peak value	Low temp. zone, -100°C	Room temp. zone, 25°C	High temp. zone, 75°C	β Transition	α Transition	
												β Transition, peak value
C1	9.54	8.96	8.78	7.81	8.08	7.24	0.015	0.108	0.223	82.58	-3.571	
C2	9.54	8.94	8.57	7.80	8.05	7.18	0.015	0.110	0.227	83.59	-5.183	
C3	9.54	8.95	8.09	7.80	8.03	7.14	0.015	0.114	0.234	84.50	-6.894	
C4	9.54	8.96	8.03	7.81	8.00	7.10	0.015	0.116	0.244	88.62	-7.84	

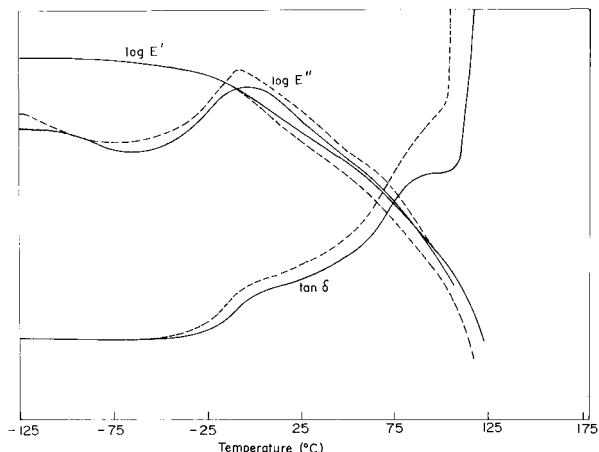


Figure 1 Loss modulus, storage modulus, and $\tan \delta$ curves for irradiated and nonirradiated systems incorporating 10 phr EVA. Nonirradiated: dashed line; irradiated: solid line

α transition

The α transition peak also follows the similar trend of decreasing peak temperature with increasing EVA content. The α transition temperature is observed from $\tan \delta$ peak. An abrupt increase in α transition temperature is observed on exposure to radiation. For composition incorporating 10 phr EVA, the α transition temperature for the nonirradiated control system is 50.26°C, which increases to 82.58°C on exposure to radiation. Other compositions also follows similar trend of increasing α transition temperatures on exposure to radiation.

Log E'' moduli values

The log E'' moduli values for the nonirradiated systems are presented in Table II. While maxima in the loss moduli E'' decreases with addition of EVA, the value of loss moduli E'' at the peak increase with addition of EVA. For composition incorporating 10 phr EVA, log E'' is 8.11 Pa while composition incorporating 20 phr EVA has log E'' 8.14 Pa. Composition incorporating 30 and 40 phr EVA has a log E'' value 8.18 and 8.20 Pa, respectively. For the irradiated systems, peak values of log E'' are presented in Table III. On exposure to radiation, a slight decrease in loss moduli values is observed. For all the compositions, log E'' curves become broader on exposure to radiation (Figs. 1–4).

Log E' moduli values

The values of Log E' moduli are presented in Tables II and III for nonirradiated control and irradiated systems respectively. Log E' moduli values were determined for three zones: low temperature zone (–100°C); room temperature zone (25°C); and high temperature

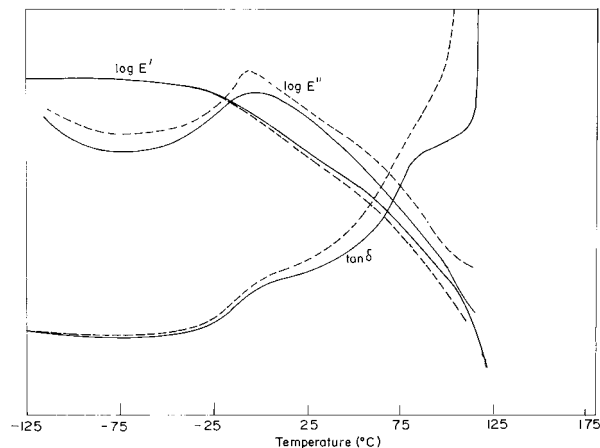


Figure 2 Loss modulus, storage modulus, and $\tan \delta$ curves for irradiated and nonirradiated systems incorporating 20 phr EVA. Nonirradiated: dashed line; irradiated: solid line.

zone (75°C). As observed from the table, on addition of EVA, no change in log E' moduli values in the low temperature zone is observed, but in the high temperature zone moduli values decreases with increasing EVA loading ratios. In case of irradiated systems, for the low temperature zone, no significant change in Log E' values is observed while for room and high temperature zones, the value of Log E' is higher for irradiated systems.

Tan δ values

The value of $\tan \delta$ for the entire range of nonirradiated control systems are presented in Table II. $\tan \delta$ increases on addition of EVA. $\tan \delta$ values were also determined for three temperature zones, i.e., at –100, 25, and 75°C. No changes in $\tan \delta$ values were observed for low temperature zone. Values of $\tan \delta$ for irradiated systems are presented in Table III. As ob-

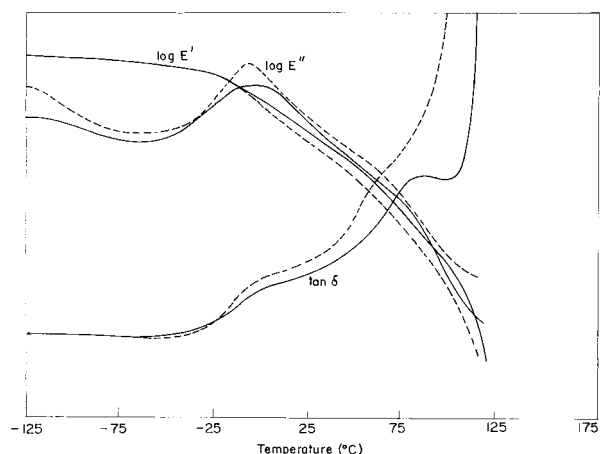


Figure 3 Loss modulus, storage modulus, and $\tan \delta$ curves for irradiated and nonirradiated systems incorporating 30 phr EVA. Nonirradiated: dashed line; irradiated: solid line

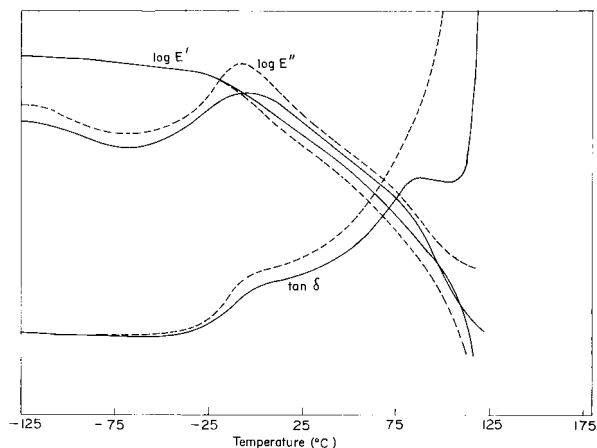


Figure 4 Loss modulus, storage modulus, and $\tan \delta$ curves for irradiated and nonirradiated systems incorporating 40 phr EVA. Nonirradiated: dashed line; irradiated: solid line.

served from the table, $\tan \delta$ decreases on exposure to radiation for room and high temperature zone, but for low temperature zone the values are comparable.

Effect of EVA content on dynamic mechanical properties

The temperatures at which the maxima in the loss moduli E'' occurs decreases on addition of EVA. These decreases in β -transition temperature is attributed to reduction in crystallinities with EVA loading ratios, which plasticize the polyethylene matrix and enhances the molecular motions of the amorphous phase, leading to lower T_g . An increase in loss moduli $\log E''$ values is observed with EVA loading ratios, which is attributed to increased amorphous phase, as loss moduli is a property of the amorphous phase, an increase of amorphous phase leads to higher $\log E''$ values.

There is a decrease in α transition temperatures and $\log E'$ moduli values with EVA loading ratios, which is attributed to reduction in crystallinity (Table IV) and plasticization of the matrix on addition of EVA. $\tan \delta$ increases with EVA loading ratios, and is attributed to the increase in loss moduli E'' and decrease in storage moduli E' . $\tan \delta$ being ratio of E''/E' increase on addition of EVA.

Effect of radiation dose on dynamic mechanical properties

An increase in β transition temperature on exposure to radiation is a consequence of the combined effects of increased crystallinities, and crosslinking in amorphous regions. All the peaks broaden on exposure to radiation (Figs. 1–4). This broadening of viscoelastic transition peak is attributed to the presence of an increased range of order and due to cage effect pro-

vided by degraded low molecular weight chains and the crosslinked three-dimensional network structure. The broadening of the viscoelastic transitions of the irradiated system infer enhanced micro heterogeneity of the matrices. The radiation crosslinking of the compositions of study is chemically complex, since in the system is present an elastomer, which may also consumed during irradiation to form crosslinked network with low-density polyethylene. A number of reactions including some chain scissions, polymerization, nucleation, and crystallization in conjunction with the predominant crosslinking reaction are expected to take place, resulting in different segmental environments, which are caged in between the dense network structure. The effect of these segmental environments is, however, overshadowed and restricted by the presence of dense crosslinks network formed upon irradiation. The crosslinks formed act as matrix anchors within which uncrosslinked chains and degraded chains of varying molecular weights are present. Both of these factors broaden the transition peaks. A decrease in loss moduli E'' values on exposure to radiation is attributed to increased crystallinity on exposure to radiation. Loss moduli as a property of the amorphous phase decreases on exposure to radiation.

The α peak shifts to higher temperature on exposure to radiation. This increase in α transition temperature on exposure to radiation is a consequence of straining effect of crosslinks formed on the molecular motions. The α transition results are due to the motions of interfacial portions between crystalline and amorphous regions (i.e., the molecular folds, loops etc.). Crosslinks formed between the chains restrict the motion of the molecules and hence more energy is required for effecting the α transition. The results are in good agreement with the literature.^{19,20}

Storage moduli E' increase on exposure to radiation for high temperature zone. This increase in storage moduli values is attributed to the hindrance caused by crosslinks for molecular motions. Moreover, crystallinity increases on exposure to radiation, which also has effect on storage moduli. The effects are prominent above T_g .¹⁹ A decrease in $\tan \delta$ values above T_g are observed on exposure to radiation, which is quite obvious as on exposure to radiation storage moduli E' increases while loss moduli E'' decreases.

TABLE IV
Degree of Crystallinity Values of Irradiated and Nonirradiated Control Systems

Ser. no.	Compositions	Control system	Irradiated system
1	C1	15.84	18
2	C2	14.71	16.7
3	C3	10.68	13.33
4	C4	9.07	11.56

CONCLUSION

Polyethylene and ethylene vinylacetate copolymers irradiated by electron beam were characterized for dynamic mechanical analyses. On addition of EVA, a decrease in transition temperature is observed, which is attributed to decreased crystallinity of the system. An increase in transition temperatures on exposure to radiation is attributed to crosslinking in polyethylene matrix, which leads to a long-range order and hence increase in energy for transition to occur. All the peaks get broaden on exposure to radiation, which is attributed to cage effect provided by degraded low molecular weight chains and the crosslinked three-dimensional network structures.

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