EFFECT OF GAMMA RADIATION IN VACUUM ON THE TENSILE PROPERTIES OF POLYMER FILMS

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SUMMARY

The tensile properties of polymer films have been measured in air after the films were exposed to gamma radiation in vacuum. The dose rate was approximately 1.6 megarads per hour for doses to 2,000 megarads at a pressure of 10^{-6} torr. Four 0.001-inch-thick films were tested: poly(ethylene terephthalate) or PETP; poly(cyclohexylenedimethylene terephthalate) or PCTP; poly(vinylidene flouride) or PVF_2; and a polyimide or PI. The yield strength, tangent modulus, tensile strength, and elongation at break were obtained from the tensile tests. The average value and standard deviation of each property are given, based on the results of twenty-five tests at each dose. The data show the effect on the tensile properties of chain scission and cross linking, and indicate the useful dose range of the films subjected to ionizing radiation.

INTRODUCTION

The increasing use of polymers for aerospace mechanical and structural applications has exposed the polymers to a wide range of often damaging environments. One of the most damaging to organic materials is that of ionizing radiation (ref. 1). In aerospace applications (and some terrestial applications as well), the polymers may be subjected to

both ionizing radiation and vacuum and still have to function as a load-bearing element in a mechanism or structure. It is therefore, of practical interest to know what effect such vacuum-radiation environment has on the mechanical properties and how such properties vary with increasing radiation dose.

The polymers were investigated in film form because extensive use has been made of films in several aerospace structures (ref. 2, 3, 4). Two polyesters, a fluorocarbon, and a polyimide were exposed to gamma radiation in a vacuum and subsequently subjected to tensile tests in air. This paper will present the results of those tests.

DESCRIPTION OF MATERIALS AND TESTS

Materials

Table I lists the polymer films which were investigated. All films were approximately 0.001-inch-thick, and all except the polyimide were crystalline. The PETP and PCTP have similar molecular structures, the difference being, that the latter has an additional six member ring (ref. 5). The polyimide is representative of the aromatic, heterocyclic polymers which possess high temperature and radiation stability (ref. 6).

Tests

The films were cut into 0.5-inch-wide strips approximately 6 inches long, placed in Pyrex tubes, and degassed for 3 days at 122°F (50°C) and 10^{-6} torr. After degassing, the tubes were sealed at 10^{-6} torr and irradiated in a cobalt-60 gamma radiation cell at a dose rate of 1.6 megarad/hr and at a temperature of 117°F (47°C). Following irradiation, the sealed tubes

were annealed at 185°F (85°C) for 16 hours before they were opened. In the cases in which the film was not tested immediately after the tube was opened, the film was stored under argon until it could be tested.

Tensile tests were performed on the film strips at room temperature in a normal atmosphere. The strips were secured in the testing machine grips which were located 3 inches apart. The cross head was deflected at a rate of 2 inches per minute, resulting in a strain rate of 0.667 inch per inch per minute. From the stress-strain curve so obtained, it was possible to determine the tangent modulus of elasticity, the 0.2-percent off-set yield strength, the tensile strength, and the elongation at break.

RESULTS AND DISCUSSION

The results of the tensile tests of the gamma-irradiated film are listed in Tables II-VI and plotted in figure 1. Each value is the average of 24-26 tests and one standard deviation follows the $\pm$ sign.

Figure 1(a) shows the change of tensile properties relative to the control value for the PETP film. (Note that the dose is plotted on a logarithmic scale.) The control values were obtained on film which had been subjected to the same outgassing and thermal treatments as the irradiated film. Figure 1(a) shows the results of three series of tests of film which were irradiated at different times over a six month period. As a result, there is considerable scatter in the data even though each data point is the average of approximately 25 tests (see Table II).

Figure 1(a) shows that the degradation in the tensile properties is slight for doses up to approximately 50 megarads. At 100 megarads,

however, both the tensile strength and elongation drop rapidly. By contrast, the yield strength and modulus show relatively little change for doses up to 174 megarads. The changes shown in figure 1(a) are comparable to those reported in references 7 and 8 for PETP irradiated in air.

The effect of vacuum, radiation, and temperature was investigated by placing an oven inside the gamma cell. By this means the film could be heated and irradiated while it was in a vacuum. Table III lists the tensile properties after the film was heated under vacuum for times up to 600 hours, and after heating and irradiating simultaneously for doses up to 153 megarads. The film was heated to 212°F (100°C), a temperature which is definitely above the glass transition temperature of PETP (Table I). It is apparent from Table III that heat and vacuum together decrease the tensile strength and elongation, increase the tangent modulus, and have little effect on the yield strength, compared to the control values listed in Table II. When the PETP film was subjected to both heat and radiation under vacuum, the tensile strength and elongation were further reduced, but the yield strength and tangent modulus first increased and then decreased. Although the absolute values of the tensile properties were decreased, the relative change in the properties was not affected by exposure of the film to the elevated temperature during irradiation. It is possible, of course, that the temperature annealed some of the radiation damage.

The effect of gamma radiation on the tensile properties of PCTP is listed in Table IV and illustrated in figure 1(b). The trends here are much more clear because there are fewer data compared to PETP. Both the tensile strength and elongation show a moderate decline for doses to approximately 50 megarads after which the properties decrease rapidly.

By contrast, the yield strength and tangent modulus increase for doses up to 200 megarads.

The variation of tensile properties of PVF_2 film for doses of 100 to 1,000 megarads is listed in Table V and illustrated in figure 1(c). It is apparent that all the properties increase by 20 to 40 percent during the first 100 megarads of radiation except for the elongation which decreases by 20 percent. The response of the tensile strength and elongation is similar to the response which is reported in reference 9, and has been attributed to molecular cross linking (ref. 10).

The test results of the PI film are listed in Table VI and plotted in figures 1(d) and 1(e). The film was irradiated in both air and vacuum and it was heated to 347°F (175°C) for the 1,500 megarad dose. Gamma radiation in vacuum has little effect on the tensile properties except for the increase in tensile strength and elongation at the higher doses. The elevated temperature decreases the yield strength and modulus but increases the tensile strength and elongation. When the PI film was irradiated in air, all of the properties except the elongation increased initially before decreasing, a response which is similar to that of the PVF_2 film which was irradiated in vacuum. The elevated temperature during irradiation in air decreased all the properties except the tensile strength.

In all polymers there is a general relationship, as shown schematically in figure 2, that the physical properties increase with the molecular weight (ref. 11). A polymer must have a certain minimum molecular weight, such as that indicated by A, in order to have useful mechanical properties. Above molecular weight A, the mechanical properties steadily increase until

the molecular weight B, after which the properties increase at a lower rate. If a polymer of molecualr weight B undergoes a 50 percent increase in molecular weight to C, then the mechanical properties increase by some 25 percent. By contrast, a 50 percent decrease from B to A would result in a 90 percent loss of mechanical properties. Although these figures do not pertain to any one polymer, they are illustrative of the extensive mechanical property changes which can accompany molecular weight changes.

The molecular weight of a polymer can be changed by ionizing radiation such as gamma radiation (ref. 12). The radiation can decrease the molecular weight by breaking the main molecular chain, or it can increase the weight by promoting cross linking between the chains. If either cross linking or chain scission only were taking place, then the properties might vary as shown schematically in figure 3. Assuming that a polymer starts with a molecular weight of B, then the radiation-induced cross linking increases the molecular weight so that the mechanical properties increase at a continuously decreasing rate. However, if the radiation causes chain scission, then the molecular weight decreases as do the mechanical properties. It is likely that both cross linking and chain scission take place to some degree when a polymer is irradiated. Consequently, the measured mechanical properties may increase and then decrease with increasing dose as shown in figure 3.

There are factors other than molecular weight which can influence the response of a polymer to ionizing radiation, factors such as the degree of crystallinity, the rate of reforming of broken bonds, and the extent of molecular orientation (ref. 13). In addition, the tensile properties are not completely independent of one another. For example,

as the tangent modulus increases, the elongation may decrease because the higher modulus prevents a wide redistribution of stress around the inherent flaws in the film. As a result, the film may break at a low average strain and appear to be brittle even though it is still flexible.

Despite the various complicating factors, there are general relationships which appear in the data. For example, the tangent modulus and yield strength either increase together or decrease together. As the absorbed dose increases, the yield strength and tangent modulus first decrease and then increase for the PETP and PCTP film. For the PVF_2 and PI film, the sequence is reversed. Again, the vacuum irradiated PI film is the exception. In contrast to the elastic properties, the ultimate properties of tensile strength and elongation generally decrease for the range of absorded doses which were investigated. The decrease is shown in figure 4 where the arrows indicate increasing dose. At the lower doses (100 to 500 megarads), the tensile strength of the PVF_2 and PI film apparently increases even though the elongation decreases.

The change of tensile properties of the polymer films is illustrated by the generalized stress-strain curves of figure 5 where the curves are numbered 0, 1, 2 to indicate zero, low, and high doses. The PETP and PCTP films change as shown in figure 5(a). The predominant molecular change for the PETP is main chain scission (ref. 14 and 15). The changes in the PVF_2 film (which undergoes cross linking) and the PI film (irradiated in air) are illustrated

in figure 5(b). The curves in figure 5 are highly generalized and the changes are exaggerated for purposes of clarity. However, it appears that the curves of figure 5(a) are characteristic of polymer films which undergo chain scission during irradiation, and those of figure 5(b) are typical of films which experience radiation cross linking.

CONCLUDING REMARKS

Thin polymer films, approximately 0.001-inch-thick, have been exposed to gamma radiation in vacuum and the tensile properties have been measured in air. Because ionizing radiation can promote both chain scission and cross linking, the mechanical response can be complicated. In general, however, the chain scission polymers and the cross linking polymers showed distinctly different stress-strain curves as a function of absorbed dose. The elastic properties (tangent modulus and yield strength) first decreased and then increased with dose for the chain scission polymers whereas the sequence was reversed for the cross linking polymers. The ultimate properties (tensile strength and elongation) generally decreased over the range of doses which were investigated. Both the fluorocarbon and the polyimide film were essentially unchanged by doses which were far in excess of those which destroyed the useful mechanical properties of the polyester films.

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TABLE I - PROPERTIES & CHARACTERISTICS OF POLYMER FILMS

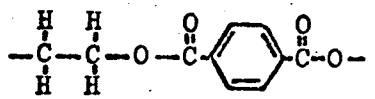
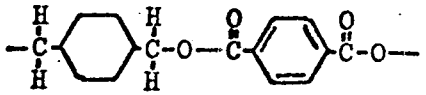
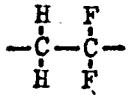
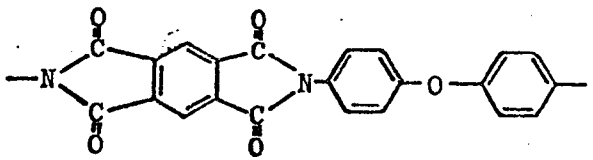
Name and Abbreviation	Specific Gravity	Glass Transition Temperature, °F(°C)	Molecular Repeat Unit
Poly(ethylene terephthalate), PETP	1.395	185 (85)	
Poly(cyclohexylene dimethylene terephthalate), PCTP	1.226		
Poly(vinylidene fluoride) PVF_2	1.76	-31 (-35)	
Polyimide, PI	1.42		

TABLE II - THE EFFECT OF GAMMA RADIATION IN VACUUM ON THE TENSILE PROPERTIES OF 0.001-INCH-THICK POLY(ETHYLENE TEREPHTHALATE) (PETP) FILM

Dose, Megarads	Series			Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, Percent
	1	2	3				
Control	X			$(11.1 \pm 0.8) \times 10^3$	$(22.2 \pm 2.4) \times 10^3$	$(5.67 \pm 0.39) \times 10^5$	156±28
Control		X		(11.7±0.5)	(22.2±1.9)	(5.98±0.23)	139±30
Control			X	(11.6±0.5)	(22.8±3.4)	(5.63±0.35)	150±36
2		X		(11.1±0.4)	(23.4±1.5)	(5.74±0.23)	173±17
4		X		(10.7±0.5)	(20.7±2.1)	(5.66±0.24)	136±32
4			X	(11.6±0.4)	(26.8±1.5)	(6.48±0.29)	115±16
5	X			(11.9±0.5)	(21.2±2.6)	(5.21±0.25)	135±11
8			X	(11.1±0.7)	(26.6±2.2)	(6.64±0.34)	119±27
9		X		(10.4±0.7)	(20.1±0.9)	(5.55±0.24)	138±16
10	X			(11.1±0.5)	(22.9±1.5)	(5.44±0.13)	170±15
13		X		(11.5±0.5)	(20.4±1.9)	(5.47±0.33)	141±27
14			X	(11.0±0.5)	(20.9±2.1)	(5.68±0.25)	157±35
27		X		(11.7±0.6)	(20.6±1.6)	(5.65±0.28)	154±23
48			X	(11.2±0.5)	(17.3±2.0)	(5.76±0.30)	120±52
89	X			(12.6±0.5)	(17.4±0.6)	(5.48±0.28)	121±19
167			X	(11.5±0.8)	(14.1±1.0)	(5.82±0.29)	18±17
174	X			(10.7±2.6)	(12.8±4.4)	(6.16±0.39)	4±2

TABLE III - THE EFFECT OF 212°F (100°C) TEMPERATURE AND GAMMA RADIATION IN VACUUM ON THE TENSILE PROPERTIES OF 0.001-INCH-THICK POLY(ETHYLENE TEREPHTHALATE) (PETP) FILM

Dose, Megarads	Number of Hours Exposed	Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, Percent
Control	66	$(11.4 \pm 0.6) \times 10^3$	$(16.6 \pm 2.2) \times 10^3$	$(7.02 \pm 0.27) \times 10^5$	37±36
Control	92	(11.2±0.6)	(16.8±2.0)	(6.36±0.36)	56±40
Control	167	(11.2±0.6)	(18.0±2.6)	(6.75±0.41)	62±38
Control	498	(11.0±0.6)	(16.0±1.2)	(6.47±0.30)	53±26
Control	600	(11.6±0.4)	(18.6±2.4)	(6.99±0.19)	67±37
72	48	(11.4±0.8)	(17.4±1.8)	(7.06±0.46)	50±27
119	76	(12.0±1.0)	(15.6±2.4)	(6.99±0.32)	4±1
153	98	[a](10.0±2.0)	[a](11.2±2.0)	[a](6.76±0.39)	[a]2±1

[a] Average of Ten Tests.

TABLE IV - THE EFFECT OF GAMMA RADIATION IN VACUUM ON THE TENSILE PROPERTIES OF 0.001-INCH-THICK POLY(CYCLOHEXYLENEDIMETHYLENE TEREPHTHALATE) (PCTP) FILM

Dose, Megarads	Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, Percent
Control	$(8.9\pm0.4)\times10^3$	$(21.1\pm2.2)\times10^3$	$(3.59\pm0.20)\times10^5$	88±53
10	(8.4±0.5)	(17.3±1.6)	(3.46±0.15)	81±18
20	(8.7±0.6)	(16.9±1.5)	(3.63±0.26)	75±13
51	(9.3±0.3)	(16.9±1.1)	(3.80±0.11)	72±13
102	(8.8±0.8)	(14.0±0.8)	(4.03±0.26)	39±12
203	(9.7±0.5)	(12.9±1.2)	(4.13±0.12)	16±7
508	[a](1.1±0.6)	[a](1.1±0.6)	---	[a] <1

[a] Average of Ten Tests.

TABLE V - THE EFFECT OF GAMMA RADIATION IN VACUUM ON THE TENSILE PREOPERTIES OF 0.001-INCH-THICK POLY(VINYLIDENE FLUORIDE) (PVF_2) FILM

Dose, Megarads	Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, Percent
Control	$(4.2\pm0.2)\times10^3$	$(6.6\pm0.4)\times10^3$	$(2.14\pm0.18)\times10^5$	13±5
102	(5.5±0.7)	(8.9±1.0)	(2.63±0.34)	10±1
202	(4.9±0.2)	(7.6±0.5)	(2.40±0.19)	9±3
645	(4.4±1.0)	(6.0±0.6)	(2.18±0.26)	8±3
1,061	(4.0±0.6)	(5.9±0.8)	(2.08±0.14)	7±3

TABLE VI - THE EFFECT OF GAMMA RADIATION IN VACUUM AND IN AIR ON THE TENSILE PROPERTIES OF 0.001-INCH-THICK POLYIMIDE (PI) FILM

Dose, Megarads	Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, Percent
Control	$(6.8\pm1.0)\times10^3$	$(20.8\pm2.6)\times10^3$	$(4.20\pm0.51)\times10^5$	87±20
		Vacuum		
500	(6.2±0.8)	(22.0±2.6)	(4.09±0.44)	96±25
1,000	(7.2±0.4)	(21.8±2.6)	(4.18±0.65)	77±26
1,500[a]	(6.0±0.6)	(23.6±2.0)	(4.07±0.24)	81±22
2,000	(6.4±0.6)	(24.4±4.2)	(4.23±0.58)	84±25
		Air		
500	(7.8±1.0)	(22.8±2.4)	(4.61±0.55)	73±27
1,000	(7.4±0.8)	(20.2±3.0)	(4.50±0.58)	60±20
1,500[a]	(6.2±0.6)	(17.4±1.6)	(4.09±0.48)	31±16
2,000	(6.8±0.4)	(17.2±1.2)	(4.05±0.18)	36±13

[a] Irradiated at 347°F (175°C).

FIGURE LEGENDS

Figure 1 - Effect of gamma radiation in vacuum on the relative tensile properties of polymer films. (a) PETP

Figure 1 - Continued. (b) PCTP

Figure 1 - Continued. (c) PVF_2

Figure 1 - Continued. (d) PI

Figure 1 - Concluded. (e) PI, irradiated in air.

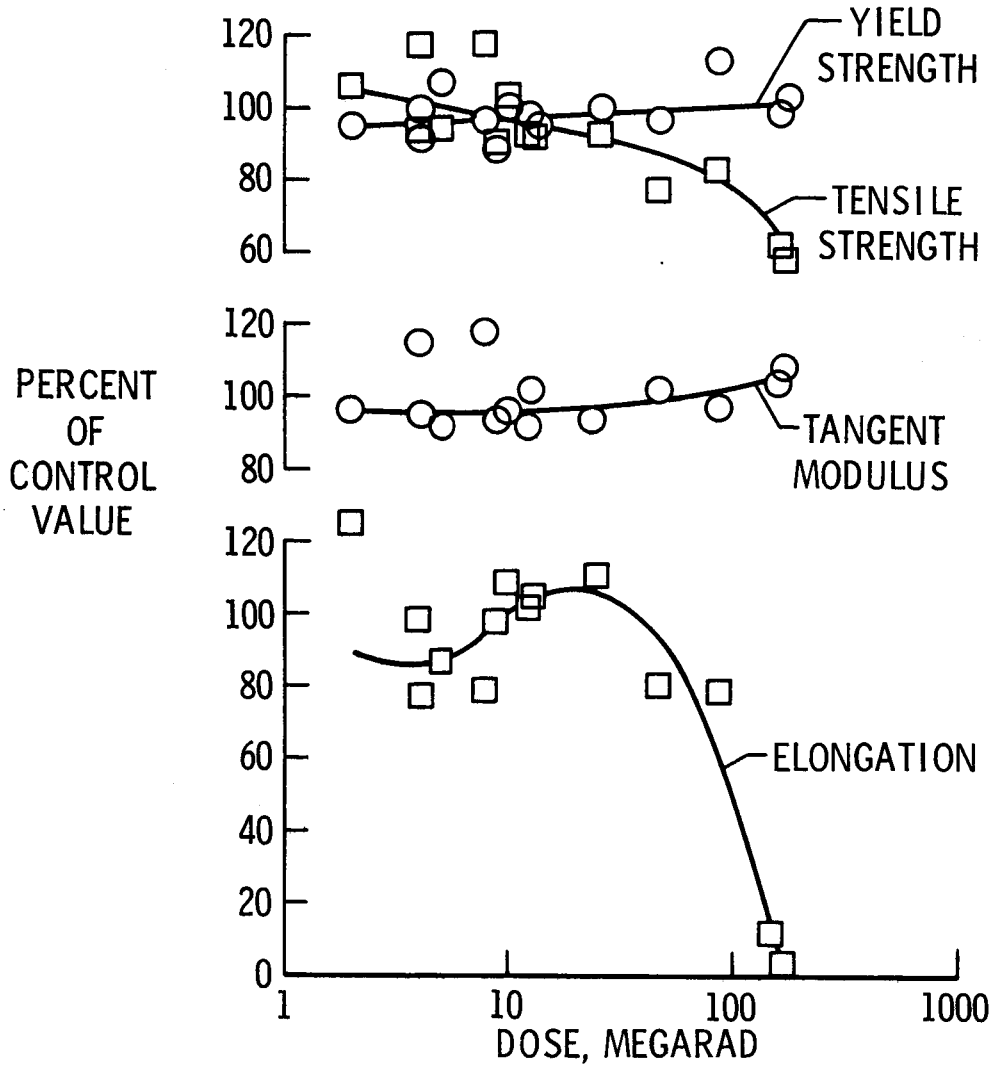
Figure 2 - Effect of molecular weight on the mechanical properties of polymers.

Figure 3 - Change of mechanical properties of polymers which undergo only cross linking or main chain scission (dashed curves). Since real polymers may experience both mechanisms, the measured mechanical properties may reflect the effect of both cross linking and chain scission (solid curve).

Figure 4 - Effect of gamma radiation on the ultimate tensile properties (tensile strength and elongation) of polymer films. The arrows indicate the direction of increasing dose.

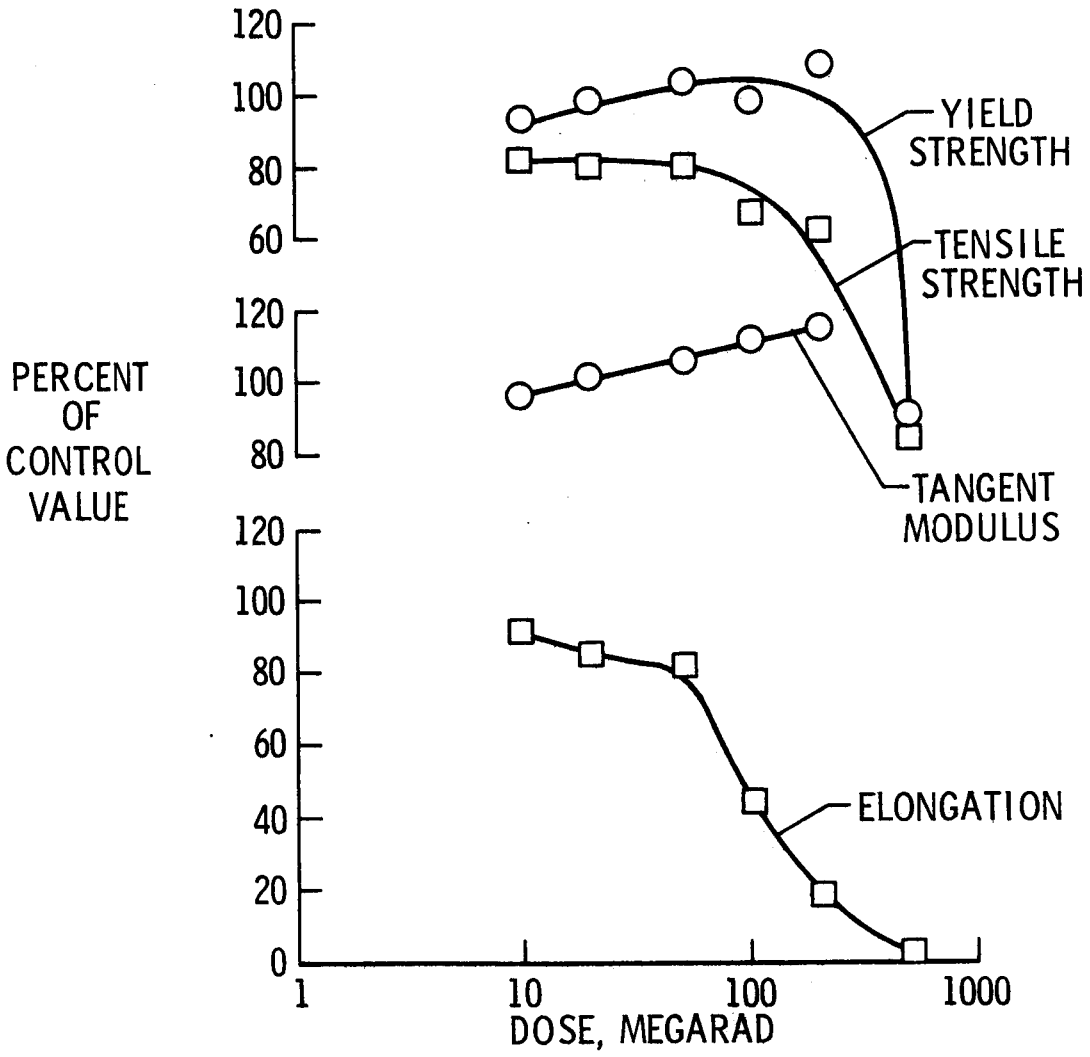
Figure 5 - Generalized tensile stress-strain curves of polymers which undergo predominantly chain scission or predominantly

cross linking during irradiation. The 0, 1, and 2 indicate zero, low, and high doses and the tick marks show the yield stress. (a) Chain scission. (b) Cross linking.



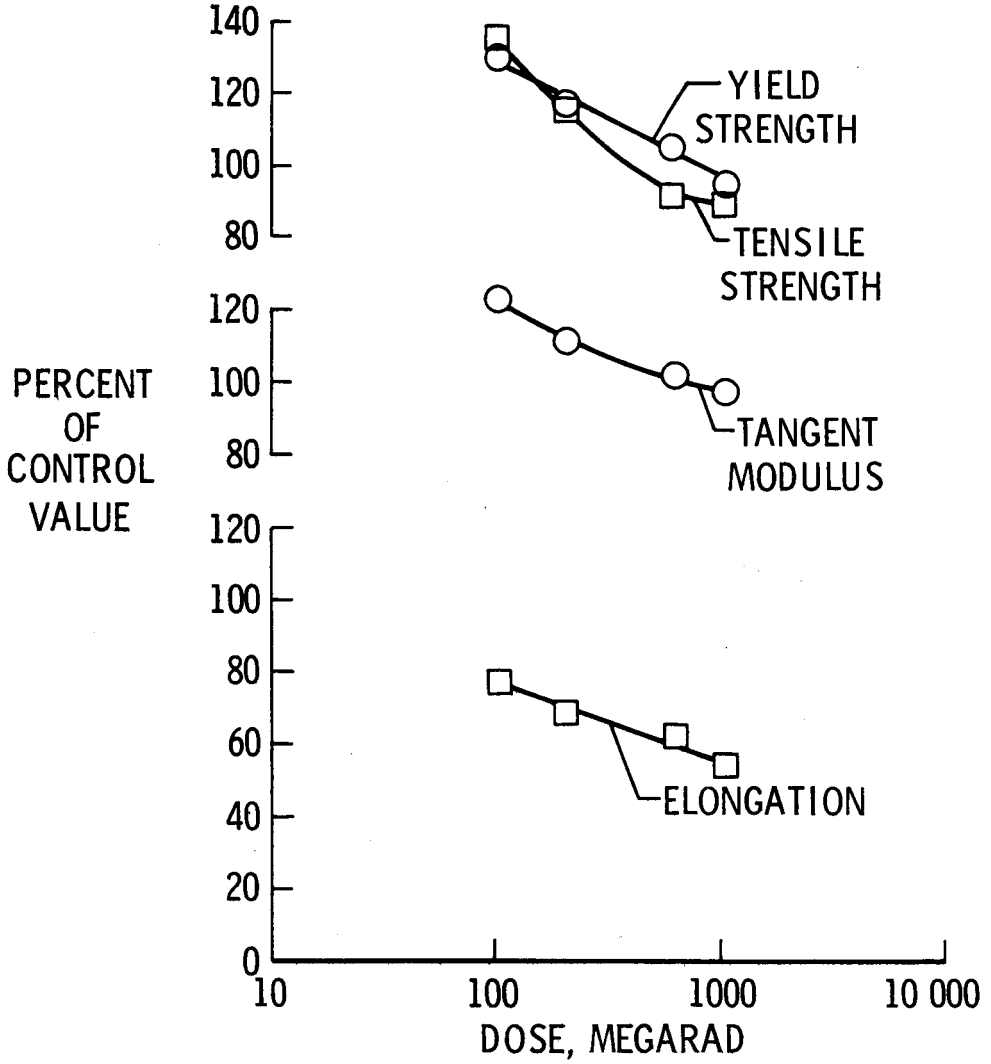
(a) PETP.

Figure 1.- Effect of gamma radiation in vacuum on the relative tensile properties of polymer films.



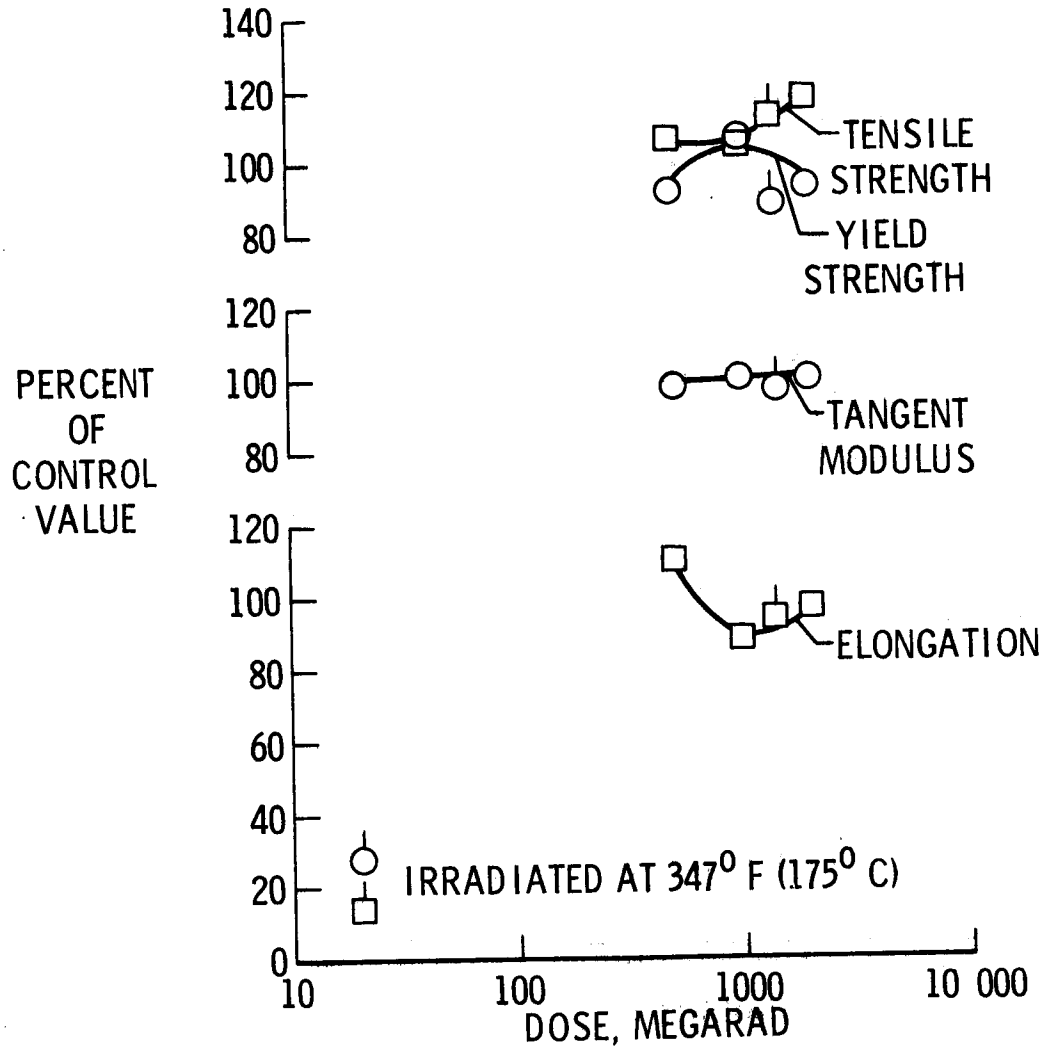
(b) PCTP.

Figure 1.- Continued.



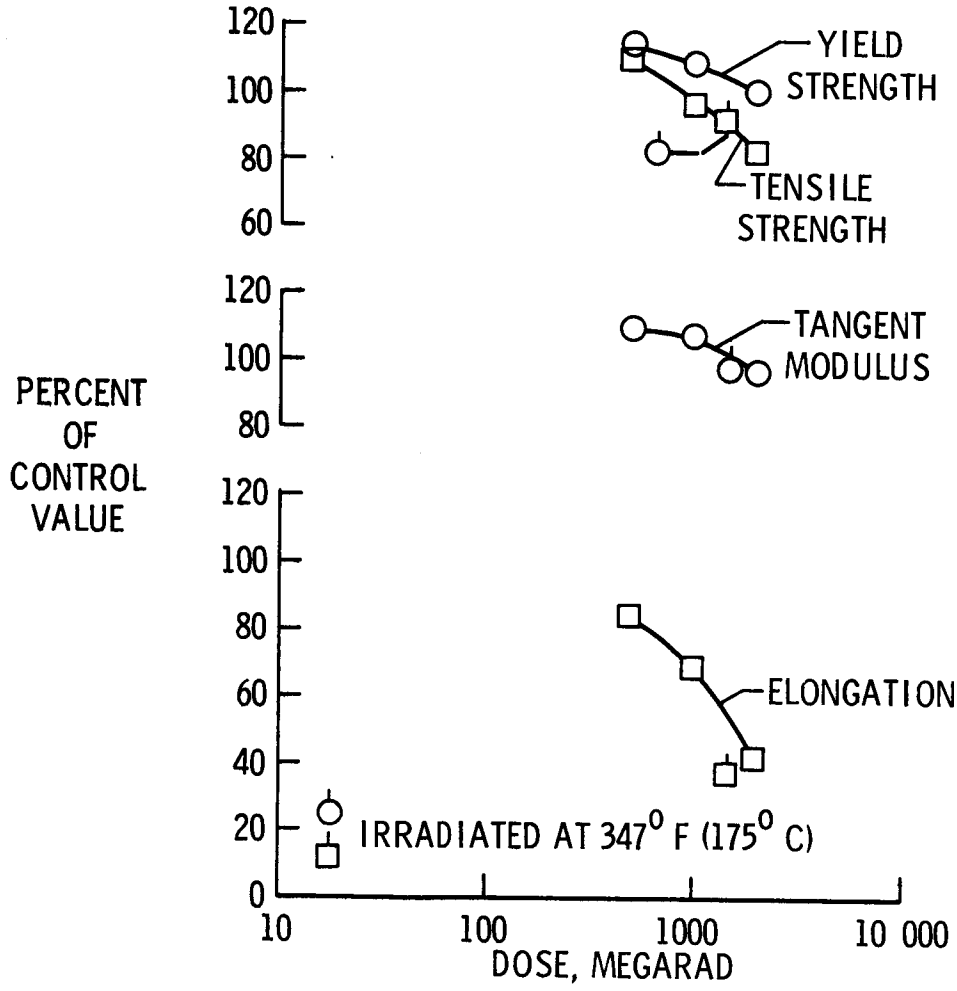
(c) PVF_2.

Figure 1.- Continued.



(d) PI.

Figure 1.- Continued.



(e) PI, irradiated in air.

Figure 1.- Concluded.

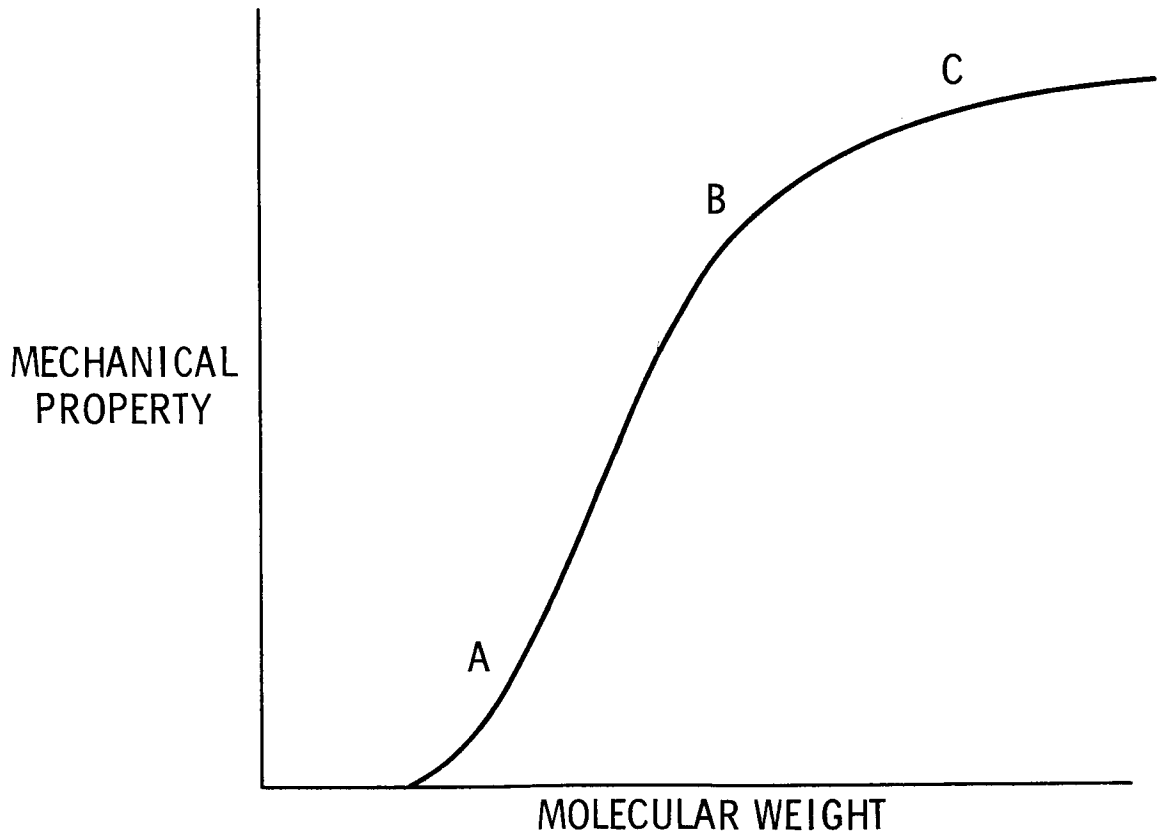


Figure 2.- Effect of molecular weight on the mechanical properties of polymers.

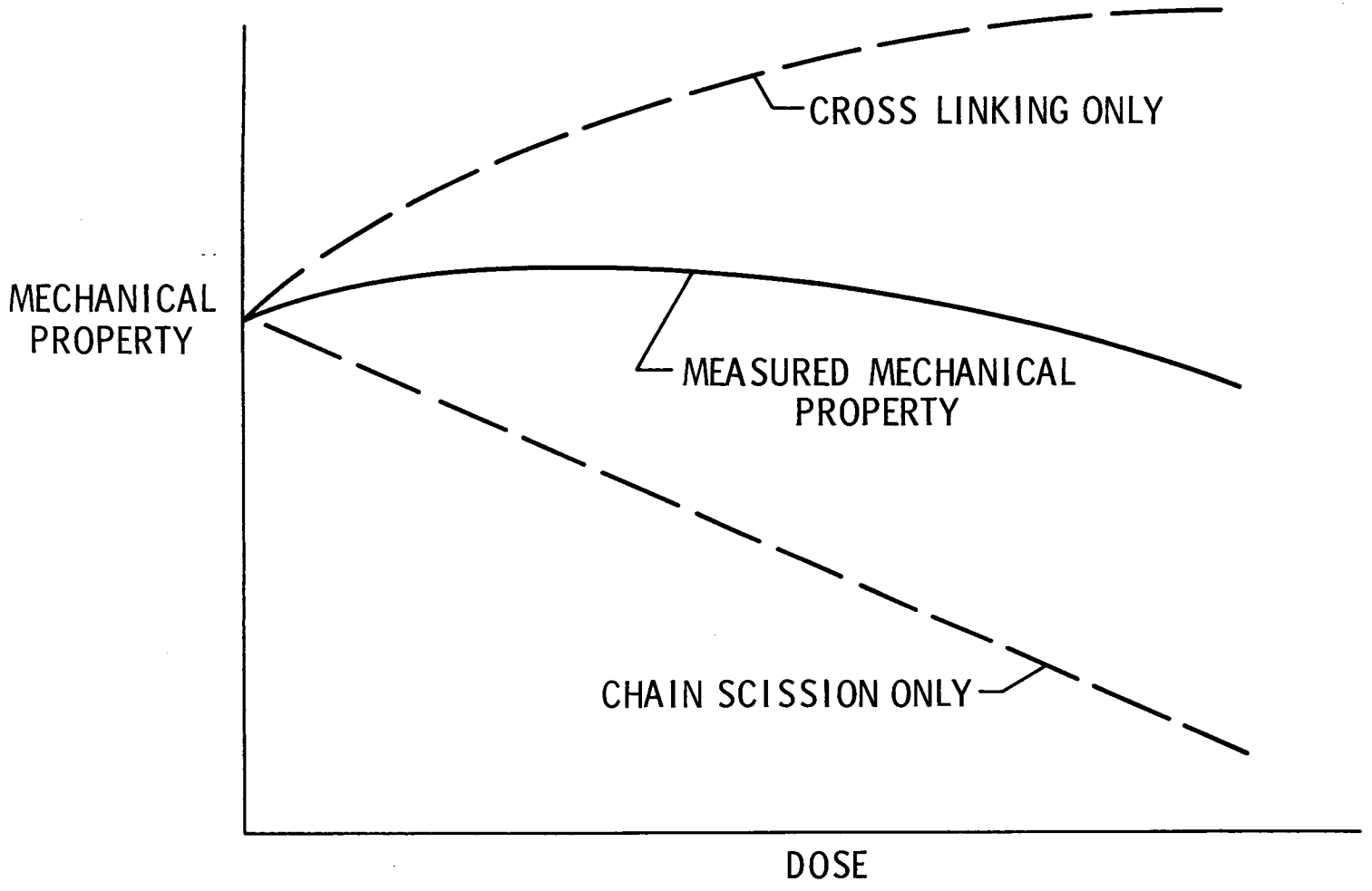


Figure 3.- Change of mechanical properties of polymers which undergo only cross linking or main chain scission (dashed curves). Since real polymers may experience both mechanisms, the measured mechanical properties may reflect the effect of both cross linking and chain scission (solid curve).

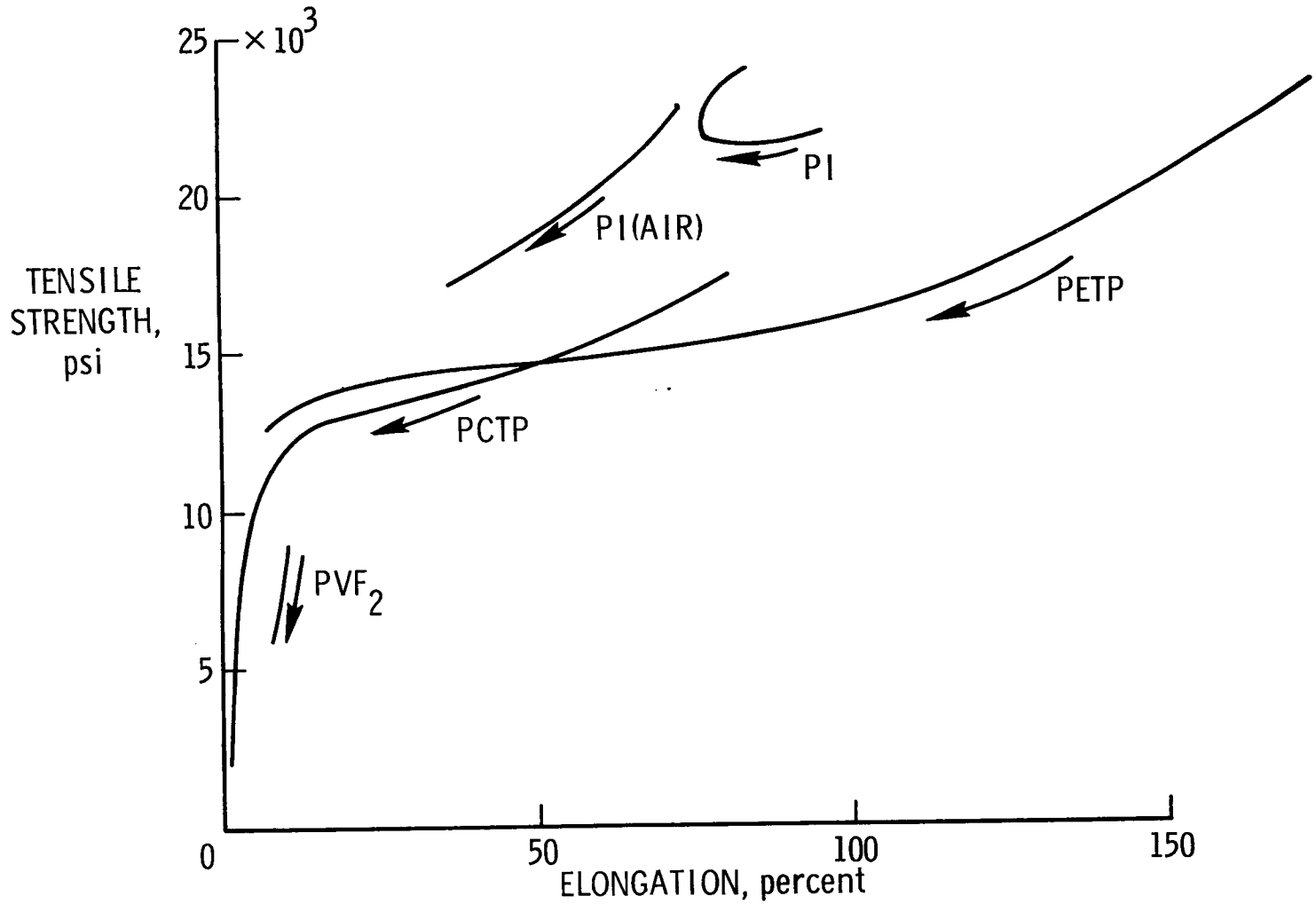
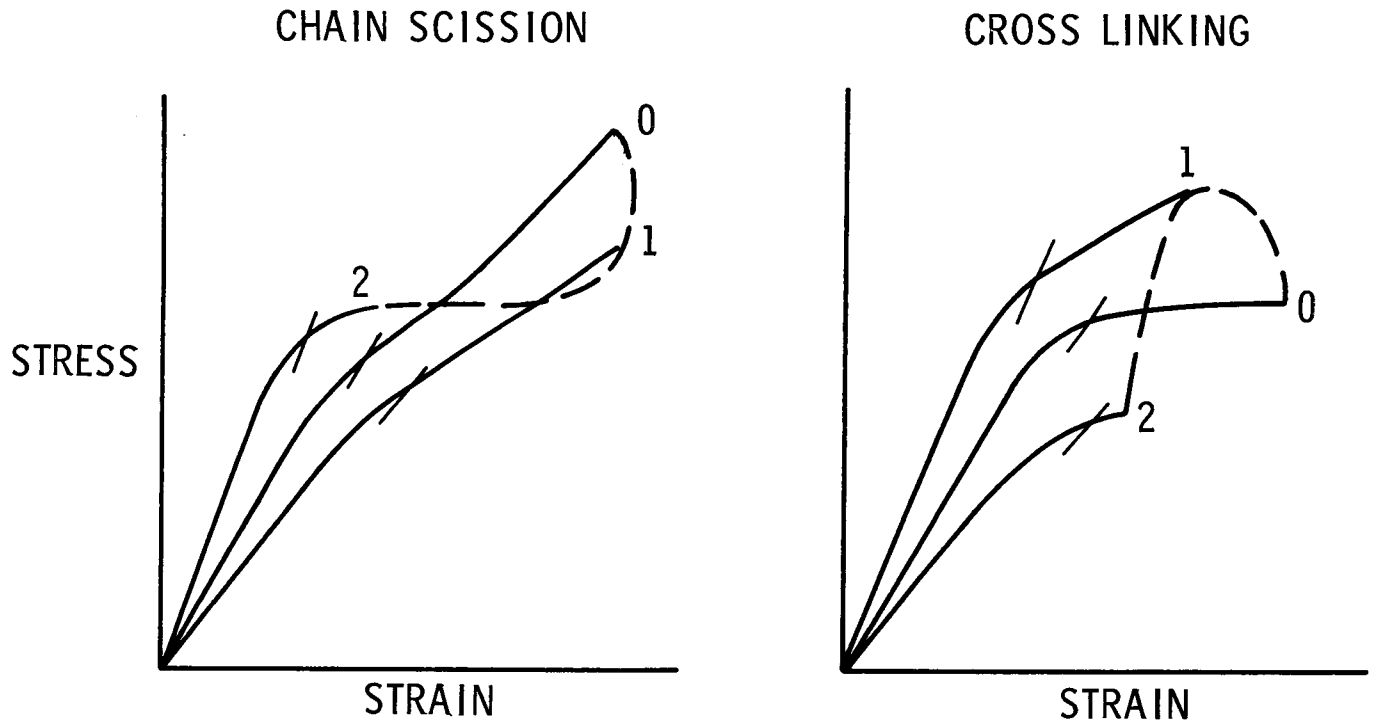


Figure 4.- Effect of gamma radiation on the ultimate tensile properties (tensile strength and elongation) of polymer films. The arrows indicate the direction of increasing dose.



(a) Chain scission.

(b) Cross linking.

Figure 5.- Generalized tensile stress-strain curves of polymers which undergo predominantly chain scission or predominantly cross linking during irradiation. The 0, 1, and 2 indicate zero, low, and high doses and the tick marks show the yield stress.