

Radiation Effects in Polystyrene*

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I. INTRODUCTION

In an earlier paper¹ the dynamic mechanical properties of polystyrene were given for frequencies near one kilocycle, and other investigators have reported results for both lower and higher frequencies.^{2,3} In a recent paper by Wall, Sauer, and Woodward⁴ the behavior of atactic and isotactic polystyrene is discussed. Only minor differences between the atactic and isotactic samples are apparent from their data for the temperature range of 80 to 370°K. Slightly above 370°K., the non-crystalline (atactic) samples began to soften to the point where the apparatus could not be used for measurements. However, the partially crystalline (isotactic) samples continued to be measurable over the range including the damping maximum and the inflection point in the dynamic modulus. Further, a second rise in damping and a subsequent decrease in modulus occurred near the reported melting point of 500°K. for crystalline polystyrene.

The large maximum in the damping value in the region of 400°K. is associated with the glass-rubber transition in the amorphous regions of the partially crystalline specimen, while the second increase in damping (475°K.) is attributed to molecular motion permitted by the melting of the crystallites. In amorphous polystyrene, the damping increases near 370°K. as the glasslike structure of the amorphous regions melts and the polymer liquefies rather than becoming rubberlike. In recent studies, efforts have been made to crosslink amorphous polystyrene by means of nuclear radiation to simulate the effect of crystallites in holding together the amorphous structure. This paper reports results obtained in experiments on the effects of radiation on dynamic mechanical properties of polystyrene.

II. EXPERIMENTAL

Polystyrene samples were turned from rods of the material as described in Reference 1. The \bar{M}_n

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for this polystyrene was reported by the manufacturer to be about 69,000 and the density was measured to be near 1.06 g./cc. In the various experiments, these rodlike specimens (4.4 in. long by 0.340 in. in diameter) were tested in a slightly modified version of an apparatus reported elsewhere by the author.⁵ The frequency range was from 500 to 1400 cycles/sec.

Irradiations were carried out at the Pennsylvania State University Nuclear Reactor Facility. Other experiments have indicated that in this facility the dose rate for polystyrene at the position of irradiation, i.e., near the core, is 0.7×10^4 ergs/g.-hr.-w.⁶ Of this, 30-40% is the result of fast neutron interactions with nuclei of the sample, largely ^1_1H , and the rest, except for slight contributions by other processes, is the result of gamma interactions.

Samples were irradiated at 100 kw. reactor power for times ranging from about 17 to 540 hr. to accumulate the radiation doses given in Table I. Specimens were placed in aluminum containers and air-sealed before being placed in position. Because of the energy deposited in the material by the nuclear radiation, the equilibrium temperature during irradiation was estimated to be 20 to 30 centigrade degrees above the temperature of the reactor pool water ($\sim 25^\circ\text{C}$). The thermal neutron flux at the irradiation position was about 0.5×10^{12} neutrons/cm.²-sec.

TABLE I
Irradiation of Polystyrene Samples

Sample no.	Radiation dose	
	ergs/g. $\times 10^{-10}$	rads $\times 10^{-9}$
1	1.2	0.12
2	3.6	0.36
3	38	3.8

III. RESULTS AND DISCUSSION

After irradiation up to 1.2×10^{10} ergs/g., the polystyrene (sample 1) no longer became liquid at

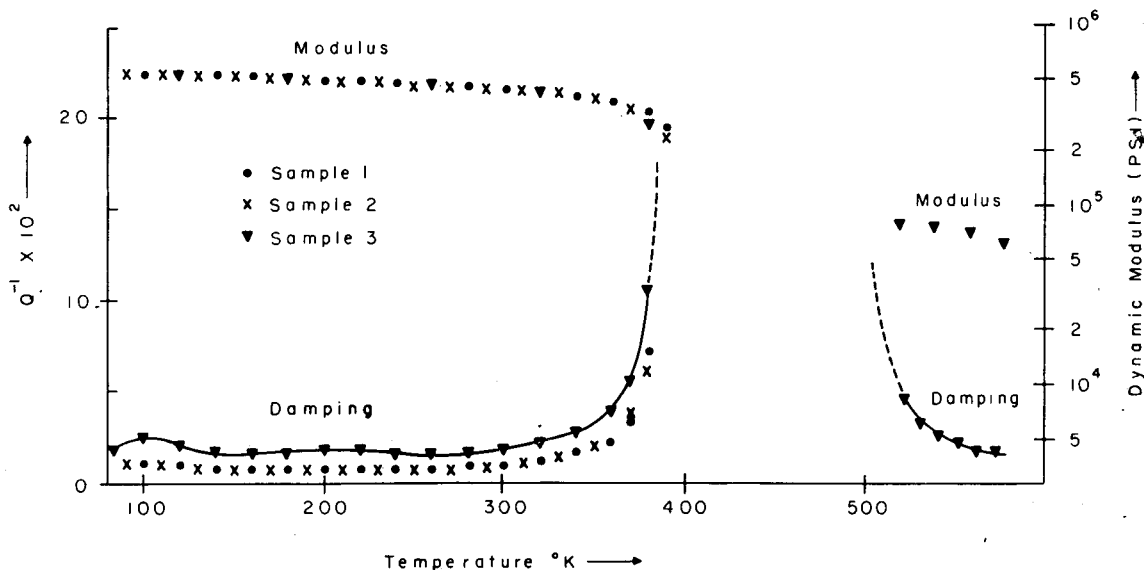


Fig. 1. Internal friction and dynamic modulus for irradiated amorphous polystyrene samples. (Dashed curve drawn to suggest damping peak.)

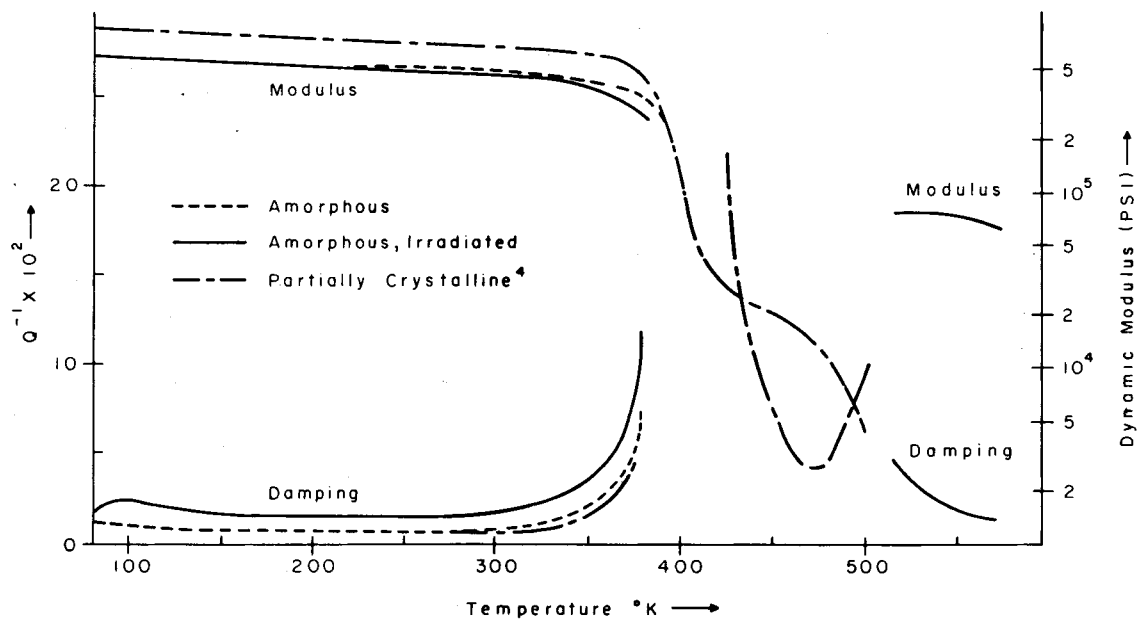


Fig. 2. Internal friction and dynamic modulus for amorphous polystyrene, irradiated amorphous polystyrene (sample 3) and isotactic, partially crystalline polystyrene (data of Wall, Sauer, and Woodward⁴). From the portions of the damping curves obtained, it appears that the peak for the amorphous, irradiated sample is roughly twice as broad as the first peak for the partially crystalline sample.

the characteristic temperature near 100°C.; however, the modulus above this point was too low to permit the self-support necessary for testing in the apparatus. Results for the internal friction and dynamic modulus of this sample are given in Figure 1; these do not differ appreciably from those given in a previous publication¹ for a sample not subjected to radiation. As in that case, a very

slight increase in the damping near 80°K. is noticeable.

From Figures 1 and 2 it is evident that the damping for sample 2 (irradiated to 3.6×10^{10} ergs/g.) differed only slightly at any temperature, if at all, from that for the unirradiated sample. The damping for sample 3, however (irradiated to 38×10^{10} ergs/g.), was distinctly different,

being higher than that of samples 1 and 2 at all temperatures between 80 and 380°K., and showing a small peak near 100°K. In addition, the internal friction of sample 3 was measurable from about 520 to 580°K. and was found to decrease gradually over this range. Near 580°K. the sample began to blister and disintegrate.

The modulus for sample 3 dropped off slightly more than that for sample 1 in the range 300–380°K. Above 500°K., where the modulus of sample 3 was again measurable, it had fallen to a somewhat lower value (7.5×10^4 psi). This value suggests a high density of radiation-induced crosslinking. The modulus remained approximately constant in this region, rather than rising with temperature in the manner of rubber. Thus, the crosslinking produced at this dose level may be of such density that the usual rubberlike behavior is strongly restricted. Below 370°K. it should be noted that both the irradiated and the unirradiated amorphous samples exhibited lower moduli than the partially crystalline, isotactic polystyrene (Fig. 2).

The data for atactic and isotactic polystyrene, as given by Wall, Sauer, and Woodward,⁴ indicate that it is the crystalline regions of the partially crystalline isotactic material that keep the polystyrene a solid beyond about 380°K. The present data indicate that a similar situation is caused in amorphous polystyrene by radiation-induced crosslinking (see Fig. 2). Although no moduli could be determined for the more lightly irradiated samples 1 and 2, above 380°K., these samples did remain solid in this region, indicating that crosslinking was sufficient to create a three-dimensional network. For the more highly irradiated sample (no. 3), the modulus at temperatures above 500°K. approached 10^5 psi. This value is rather high for an irradiation-crosslinked polymer in this temperature region.⁷ From Figure 2 it can be noted that near 400°K. the modulus for partially crystalline polystyrene dropped below 10^5 psi and continued downward with temperature rather rapidly as the crystallites melted, and that at 500°K., the reported melting point, the decrease in modulus became very sharp.

Below 370°K., the internal friction of the isotactic material of Reference 4 differs only slightly from that of the atactic, unirradiated sample, the slight relative decrease in the values for the isotactic material between 300 and 370°K. being attributable to possible restraints in the amorphous regions imposed by the crystallites (see Fig. 2).

However, the internal friction values for sample 3 (solid line) are significantly higher throughout the region 80–380°K., even showing a small peak around 100°K. Previous investigations,^{1,4,8} have given evidence that there may be a peak slightly below 80°K., and there is some evidence for this in the data on samples 1 and 2 of Figure 1. Also, other data by Sinnott⁹ indicate an internal friction peak at 40°K. with a Q^{-1} value of about 0.007 for experiments carried out at frequencies near a few cycles/sec. This peak would shift to a somewhat higher temperature at the frequencies of the experiments reported here.

The principal, amorphous-transition damping peak starting near 370°K. for the irradiated, amorphous polystyrene is much broader than for the partially crystalline material. This would suggest that the crystallites of the isotactic material are formed in such a manner that a rather uniform, narrow spectrum of relaxation times results for molecular movements in the amorphous regions. For the irradiated amorphous sample the range of relaxation times of the segments seems to be rather broad, considering that the average crosslinking density probably is high. Apparently, the irradiation, and the subsequent combinations of crosslinking and chain scission, lead to the formation of a network of segments, some of which are free to move and have a molecular weight spectrum somewhat different from that of the segments of the amorphous regions between the crystallites of the partially crystalline sample. A somewhat higher percentage of polymer segments may be free to move in the irradiated amorphous samples as compared to the partially crystalline samples, in which parts of the molecular chains are locked in the crystallites. On the other hand, dense crosslinking in the irradiated samples could severely restrain the segments at some points.

Starting at about 470°K., the internal friction of the partially crystalline material begins to rise (see Fig. 2). This is attributed by Wall et al. to the onset of polymer chain-segment motion resulting from the melting of the crystallites. This rise seems not to have occurred in the irradiated amorphous sample reported here, probably owing to the fact that crosslinks, rather than crystallites, held the material in the solid state. Instead, as the temperature was increased to 600°K. ($\sim 100^\circ\text{K.}$ above the melting point), the damping steadily decreased (solid line at lower right, Fig. 2). At 600° the specimen began to disintegrate

and no more measurements could be made. At the highest temperature ($\sim 575^\circ$), the damping approached values lower than any others obtained above 80°K . This behavior is characteristic of some other polymers as well, such as polyethylene, after they have been rather highly irradiated.

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Synopsis

Amorphous polystyrene was subjected to nuclear radiation in doses ranging from 1.2×10^{10} to 3.8×10^{11} ergs per gram. At low temperatures the internal friction of the highly irradiated polystyrene was greater than that of the unirradiated material, and beyond the glass transition, which begins near 370°K , the irradiated sample remained a solid and the internal friction decreased. Below 370°K , the dynamic modulus of the highly irradiated material scarcely differed from that of the unirradiated sample,

while beyond 500°K , it was rather high (near 10^5 psi). At low irradiation doses crosslinking occurred sufficient for the formation of a nonliquefying, three-dimensional network in the polystyrene, but no changes in the dynamic mechanical properties attributable to irradiation could be detected.

Résumé

Du polystyrène amorphe a été soumis à des doses de radiation nucléaire de $1,2 \times 10^{10}$ à $3,8 \times 10^{11}$ ergs par gramme. A basse température la friction interne du polystyrène fortement irradié est plus grande que celle du matériel non irradié, et au-delà de la transition vitreuse, qui commence près de 370°K , l'échantillon reste solide et la friction interne décroît. Il n'y a qu'un petit changement dans le module dynamique du matériel fortement irradié en dessous de 370°K , mais il reste plutôt grand (environ 10^5 psi) à des températures au-delà de 500°K . Quoique les basses doses d'irradiation suffisent pour former dans le polystyrène un réseau tridimensionnel infusible, il est impossible de décélérer des changements dans les propriétés dynamiques mécaniques de ces échantillons.

Zusammenfassung

Amorphes Polystyrol wurde Kernstrahlungsdosen von $1,2 \times 10^{10}$ bis $3,8 \times 10^{11}$ erg pro Gramm ausgesetzt. Bei niedriger Temperatur ist die innere Reibung der hoch bestrahlten Polystyrole grösser als diejenige des unbestrahlten Materials und oberhalb der bei 370°K beginnenden Glasumwandlung bleibt die Probe ein Festkörper und die innere Reibung nimmt ab. Unterhalb 370°K erfolgt nur eine kleine Änderung im dynamischen Modul des hoch bestrahlten Materials, bei Temperaturen über 500°K bleibt er jedoch ziemlich hoch (um 10^5 psi). Obgleich die Bestrahlungen mit niedriger Dosis genügen, um bei Polystyrolen ein nichtschmelzendes dreidimensionales Netzwerk zu bilden, können bei den dynamisch-mechanischen Eigenschaften dieser Proben keine Änderungen gefunden werden.

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