Effects of Sterilization Procedures on the Tensile Properties of Polycarbonate

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Synopsis

The tensile properties of polycarbonate were investigated for specimens subjected to three sterilization procedures—autoclaving, gassing, and gamma irradiation). Generally the tensile modulus decreased and the percent elongation at yield increased for all sterilization procedures. The ultimate stress was decreased by the ethylene oxide and gamma radiation procedures, while it was increased by the autoclave procedure. The total elongation at break generally increased with all sterilization procedures investigated. For repeated sterilizations, it appears that the autoclave procedures would be less detrimental to the tensile properties of polycarbonate, particularly if the maximum sterilization temperature does not exceed 260°F (127°C). Any of the sterilization methods described can probably be used on polycarbonate for a single application, although the autoclave and gamma sterilization procedures appear to be somewhat better than the gas sterilization procedures in relation to the tensile properties.

INTRODUCTION

Polycarbonate (PC) is known to be a tough, versatile thermoplastic with excellent mechanical properties, transparency, relatively high-temperature usefulness, dimensional stability, and good electric properties. Because of these properties, PC has been used in biomedical experiments, usually as a copolymer, and typically this brings up the question of sterilizability and the effects of sterilization procedures on the properties of the polymer.[1–4]

Three typical methods for sterilizing materials at present are autoclaving, gassing (ethylene oxide), and gamma irradiation. In contrast to its usual toughness, PC, in some biomedical applications, has failed under prolonged use as a biomaterial. Sterilization history may have contributed to this failure. Problems concerning the effects of sterilization, particularly gamma irradiation, on certain properties of some potential biomaterials has been discussed.[1–4] In general, gamma radiation doses above about 15 *M*rad produces polymer degradation. Also adequate degassing after ethylene oxide sterilization is needed because ethylene oxide can possibly react with certain functional groups.[2,3] Repeated sterilization with ethylene oxide, the rate of reaction with these functional groups, and the overall detriment to the mechanical properties have not been investigated in sufficient detail. Autoclave sterilization using steam can also degrade certain polymers, particularly if the glass transition temperature is significantly exceeded.[2,3] The effects of repeated steam sterilization on the rate of degradation in the mechanical properties of selected polymers have not been reported in detail. It is the purpose of this work to present and discuss some results of the effects of first sterilization and repeated sterilization procedures on the tensile properties of polycarbonate.

Journal of Applied Polymer Science, Vol. 22, 2019–2024 (1978)

0021-8995/78/0022-2019$01.00

EXPERIMENTAL

The tensile specimens were prepared by first stamping out the gross dimensions from a polycarbonate sheet which was 0.060 in. (0.15 cm) thick. Specimens were then milled to the dimensions given in ASTM D638-72.

Tensile test specimens, except those used as controls, were sterilized either by autoclaving, gassing (ethylene oxide), or subjected to a given dose of gamma radiation. All specimens, except the gamma sterilization specimens, were placed in polyethylene bags after the specified sterilization procedure until they were tested in tension.

Specimens to be autoclaved were sterilized at 250°F (121°C), 260°F (127°C), and 270°F (132°C) for 15 or 30 min at each temperature. These autoclaved specimens were subjected to either one or five sterilization procedures. Specimens were then stored in polyethylene bags until testing.

Ethylene oxide sterilization of tensile specimens consisted of either a hot or cold cycle, and both cycles were accompanied with or without a degassing procedure. In the cold cycle sterilization, the specimens were subjected to ethylene oxide for 12 hr at 85°F (29°C) and then were either removed from the chamber (nondegassing cycle) or placed under vacuum (2.5–100 mm Hg) for 12 hr at room temperature (degassing cycle). In hot cycle sterilization, specimens were exposed to ethylene oxide for 1½ hr at 140°F (60°C) followed by either the same nondegassing cycle or degassing cycle procedure as the cold cycle specimens. These specimens were taken from their polyethylene storage bags and tested 48 hr after sterilization. Repeated sterilizations using ethylene oxide were not conducted because of the results obtained after the first sterilization procedure.

Specimens sterilized with gamma radiation received doses from 1 to 100 megrads (*M*rad) from a Co^{60} gamma source. A typical radiation sterilization dose is about 3 *M*rad, but larger doses were included to investigate the degradation in the tensile properties of the polycarbonate material if subjected to repeated sterilization. After irradiation these specimens were stored in a dessicator until testing. Specimens receiving more than 100 *M*rad dose were too weak and brittle to test.

Tensile testing was conducted on a Tinius Olsen Universal Testing Machine which recorded load versus specimen elongation. The strain rate used during testing was 2.0 in./min (5.08 cm/min), and the distance between the tensile grips was the same for each specimen. Maximum tensile stress was calculated as

$$\text{maximum stress} = \frac{\text{maximum load}}{\text{cross-sectional area}}$$

and the tensile modulus was calculated from the straight line section of the stress–strain curve near the origin as:

$$\text{tensile modulus} = \frac{\text{load/original cross-sectional area}}{\text{elongation/original length}}$$

The percent elongation at yield was calculated as

$$\text{\% elongation at yield} = \frac{\text{yield elongation}}{\text{original length}} \times 100$$

RESULTS AND DISCUSSION

The tensile data listed in Table I are for the polycarbonate specimens both before and after all of the sterilization procedures used in this study. The data for the nonsterilized PC are typical values for the material. In general, both the ethylene oxide, particularly both cold cycle degassing procedures and nondegassing procedures for the hot cycle, and the gamma radiation procedures (above 10 *M*rad) appeared to reduce the maximum stress level and tensile modulus while increasing percent elongation at yield. On the other hand, the autoclaving procedure resulted in a slightly increased maximum stress level along with increased percent elongation at yield, while producing a slight decrease in the tensile modulus. Table II is a tabulation of the ratio of the given different parameters to the control value, which may help to clarify the trends.

The degassing cycle in the ethylene oxide sterilization procedures was carried out with commercially available equipment. The vacuum in the degassing cycle was not as good as that suggested by Bruck.[2,3] The vacuum levels of about 1.0 mm Hg[2,3] could not be attained with the commercial equipment used. It was felt that since the specimens were not being used in biological tests, only in mechanical testing, the degradation of the tensile properties could be observed without degassing at 1.0 mm Hg vacuum.

TABLE I
Tensile Properties of Sterilized Polycarbonate Specimens[a]

Treatment	Max stress (10^3 psi)	% Elongation at yield	Tensile modulus (10^5 psi)
Non-sterilized	11.1	12.4	1.6
Ethylene oxide, 85° F, 240 min, 1 cycle, no degassing	10.5	13.6	1.6
Ethylene oxide, 140° F, 90 min, 1 cycle, no degassing	10.8	13.3	1.5
Ethylene oxide, 85 °F, 240 min, 1 cycle, degassing	10.9	13.6	1.5
Ethylene oxide, 140° F, 90 min, 1 cycle, degassing	11.1	13.6	1.2
1 *M* rad	10.7	12.7	1.6
2 *M* rad	10.9	12.9	1.4
5 *M* rad	10.9	13.1	1.5
10 *M* rad	10.5	13.0	1.4
50 *M* rad	10.0	13.1	1.5
100 *M* rad	9.4	12.1	1.4
Autoclave			
250° F, 15 min, 1 cycle	11.5	10.8	1.2
260° F, 15 min, 1 cycle	11.8	12.4[b]	1.7[b]
270° F, 15 min, 1 cycle	11.0	13.3	1.7
250° F, 30 min, 1 cycle	11.6	12.7	1.2
260° F, 30 min, 1 cycle	11.4	13.3	1.4
270° F, 30 min, 1 cycle	11.2	12.6	1.4
250° F, 15 min, 5 cycle	11.6	13.1	1.4
260° F, 15 min, 5 cycle	11.1	13.3	1.4
270° F, 15 min, 5 cycle	10.9	13.1	1.5
250° F, 30 min, 5 cycle	11.6	12.4	1.4
260° F, 30 min, 5 cycle	11.4	13.1	1.3
270° F, 30 min, 5 cycle	11.0	12.1	1.3

[a] All data are average of 3 specimens except where noted. 1 psi = 6.895 kPa.
[b] One specimen only.

TABLE II
Summary of Tensile Properties of Sterilized Polycarbonate Specimens (Treated/Control)

Treatment	Ratio values (treated/control)		
	Max stress	% Elongation at yield	Tensile modulus
Ethylene oxide, 85° F, 240 min, 1 cycle, no degassing	0.946	1.097	1.000
Ethylene oxide, 140° F, 90 min, 1 cycle, no degassing	0.973	1.073	0.938
Ethylene oxide, 85° F, 240 min, 1 cycle, degassing	0.982	1.097	0.938
Ethylene oxide, 140° F, 90 min, 1 cycle, degassing	1.000	1.097	0.750
1 *M* rad	0.964	1.024	1.000
2 *M* rad	0.982	1.040	0.875
5 *M* rad	0.982	1.056	0.938
10 *M* rad	0.946	1.048	0.875
50 *M* rad	0.901	1.056	0.938
100 *M* rad	0.847	0.976	0.875
Autoclave			
250° F, 15 min, 1 cycle	1.036	0.871	0.750
260° F, 15 min, 1 cycle	1.063	1.000	1.063
270° F, 15 min, 1 cycle	0.991	1.073	1.063
250° F, 30 min, 1 cycle	1.045	1.024	0.750
260° F, 30 min, 1 cycle	1.027	1.073	0.875
270° F, 30 min, 1 cycle	1.009	1.016	0.875
250° F, 15 min, 5 cycles	1.045	1.057	0.875
260° F, 15 min, 5 cycles	1.000	1.073	0.875
270° F, 15 min, 5 cycles	0.982	1.056	0.938
250° F, 30 min, 5 cycles	1.045	1.000	0.875
260° F, 30 min, 5 cycles	1.027	1.056	0.813
270° F, 30 min, 5 cycles	0.991	0.976	0.813

In ethylene oxide sterilization, the percent elongation to yield increased for all treatment conditions, indicating some possible stress relief due to the treatment. The maximum tensile stress values for the ethylene oxide sterilization procedures are plotted in Figure 1. The curves in this figure are drawn only to show trends. The data, as shown in Figure 1, indicate that the ethylene oxide treatment at 80°F (29°C) is somewhat more detrimental to the maximum stress level obtained in the controls than the treatment at 140°F (60°C). It further appears that the ethylene oxide gas reacts with the polycarbonate and must be removed after sterilization. Results are somewhat different in the case of the tensile modulus. Here, the 85°F (29°C) treatment appears to be less detrimental than the 140°F (60°C) treatment. The degassing treatment appears to further reduce the modulus compared to no degassing treatment. Nevertheless, the trend for all ethylene oxide treatments appear to be a reduction in the tensile modulus values, and because of this repeated ethylene oxide sterilization were not conducted in this study.

In Figure 2, the maximum stress versus gamma dose rate is plotted. The curve is drawn to indicate the trend in the data. As is typical in many polymers, the strength decreases with dose.[2–4] A decrease is also evident in the tensile modulus. But interestingly, the % elongation at yield remains higher than the controls up to the highest dose rate used in this study (100 *M*rads). Sterilizing radiation has a degradation effect on most polymers, and it appears that above 10 *M*rads

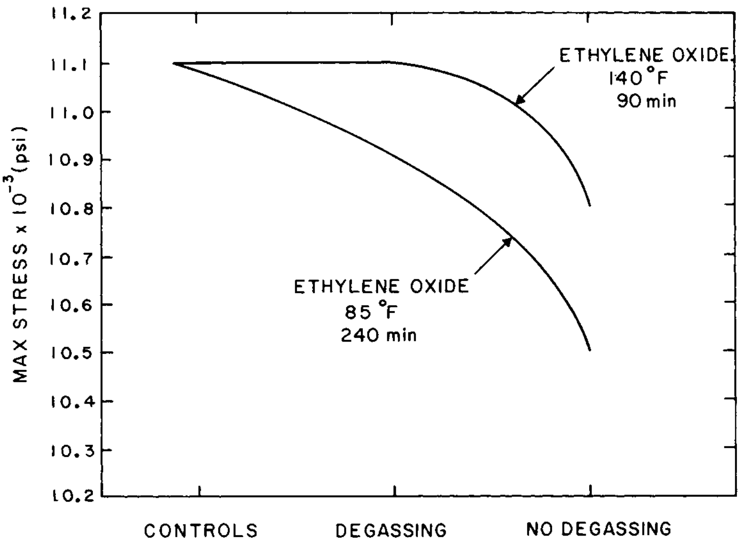

Fig. 1. Maximum tensile stress of polycarbonate vs different ethylene oxide sterilization procedures [1 psi = 6.895 kPa; $T(°F) = 9/5F(°C) + 32$].

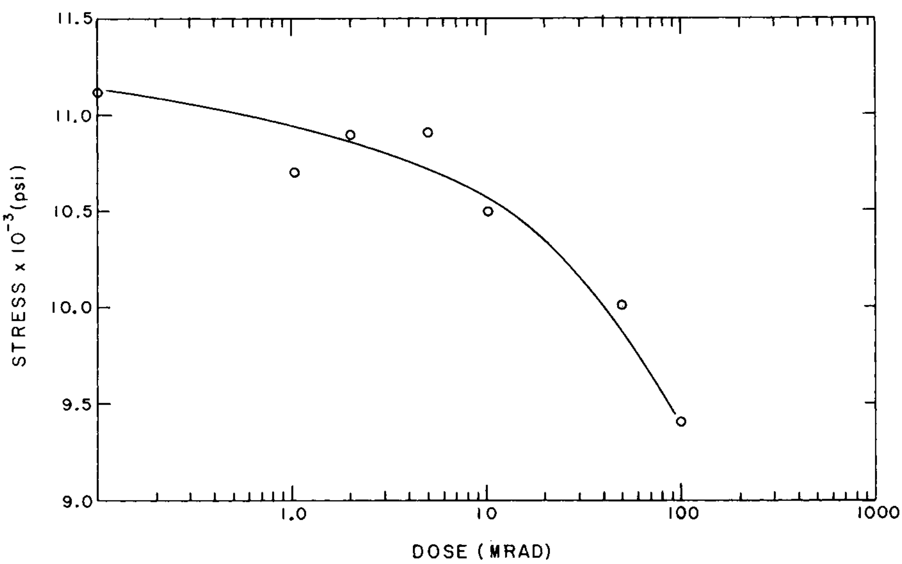

Fig. 2. Maximum tensile stress of polycarbonate vs different gamma radiation dose levels (1 psi = 6.895 kPa).

the PC begins to degrade significantly, this in concert with findings on other polymers.[2-4] From Table I it appears that at doses of 2 and 5 *M*rads the maximum stress remains near that of the control data although some slight change of color was noted. At higher doses the degradation is so severe that it may overcome recombination into lower molecular weight polymers. Gamma sterilization doses above 10 *M*rads for PC do not appear feasible.

In all of the autoclave treatments at 250°F (121°C) and 260°F (127°C), the maximum stress increased over the controls while the modulus decreased, possibly because of some stress relief in the polymer. The 270°F (132°C) treatments produced a decrease in the maximum stress and modulus. The 250°F (121°C) and 260°F (127°C) treatments appear to produce stress relief while the 270°F (132°C) treatment may be detrimental to the PC molecule. This suggests a possible critical temperature for autoclave sterilization less than or equal to 260°F (127°C). Repeated autoclave sterilization procedures (five cycles) do not appear to be detrimental to the tensile properties, particularly if the temperature is less than or equal to 260°F (127°C).

In comparing ethylene oxide, gamma radiation, and autoclave treatments, it is generally noted that all of the procedures increased the percent elongation at yield over that of the controls (Tables I and II). The ethylene oxide and gamma radiation procedures reduce the maximum stress whereas the autoclave procedure increases the maximum stress. The tensile modulus is typically reduced by all of the sterilization treatments.

SUMMARY

Polycarbonate specimens for tensile testing were sterilized by ethylene oxide, gamma radiation, and autoclave procedures. All sterilization procedures generally reduced the tensile modulus slightly and increased the percent elongation at yield. The maximum stress was decreased by the ethylene oxide and gamma radiation treatments and increased by the autoclave procedures. The total elongation at failure is generally increased by all sterilization procedures used. It thus appears from the present work that while sterilization procedures alter the maximum tensile stress, tensile modulus, and percent elongation at yield, the property changes depend largely on the sterilization procedure employed. It further appears that if the polycarbonate is going to be subjected to repeated sterilization, the autoclave procedures would be preferable, particularly if the maximum temperature does not exceed 260°F (127°C). Polycarbonate which is to be sterilized only once and then discarded after use probably could be sterilized by any of the methods described in this paper, although the autoclave and gamma radiation procedures appear to be somewhat preferable to the ethylene oxide sterilization procedure. More research concerning the effects of sterilization on the mechanical properties of biomaterials would be valuable.

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Received August 25, 1976
Revised May 2, 1977