

Evaluation of Sunlight Stability of Polyurethane Elastomers for Maxillofacial Use. II.

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Summary

The effect of selected UV stabilizers on the stability of mechanical properties of a polyurethane material, Calthane ND2300, was evaluated. The addition of UV stabilizers prolonged the service life of the systems studied but did not achieve completely satisfactory results. The tensile strength and modulus of elasticity decreased after extended exposure to UV. The rate of decrease, however, was much less for the specimens with UV stabilizers. The polyurethane system that contains a mixture of a UV stabilizer and an antioxidant is considered to be the best of the groups tested, in terms of the percentage of retention of tensile strength and modulus of elasticity. It was also found that elongation at break was increased when the duration of UV aging was increased. This phenomenon occurred in all the systems, with or without UV stabilizers, and can be understood in terms of the concepts of the fragmentation of macromolecules that resulted from UV aging. The physical appearance in conjunction with mechanical property tests are needed to ensure the successful performance of any UV stabilizer.

INTRODUCTION

Recently, studies concerning use of polyurethanes for cardiovascular prostheses¹⁻³ have broadened the scope for the possible biomedical applications of these resins. Use of these materials for maxillofacial prosthetic purposes is relatively new⁴⁻⁶ and not yet perfected; but availability, ease of processing, low cost, and a wide range of properties give polyurethanes significant potential for such purposes. The properties of polyurethanes can be largely varied simply by changing the ratio of the two major components. This versatility allows for numerous engineering applications that demand great durability and resilience.^{7,8} Since polyurethanes can be pro-

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cessed at temperatures below 100°C, they are much easier to fabricate than other current commercial materials, e.g., polyvinyl chloride (PVC).

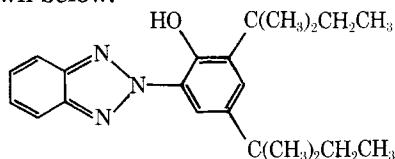
However, polyurethanes, especially the aromatic types, have one major deficiency—they degrade rapidly upon exposure to the UV wavelength range of sunlight. Discoloration of aromatic polyurethanes after UV exposure has been greatly reduced through the incorporation of aliphatic polyurethanes,^{4,5,7,8} but deterioration of the physical and mechanical properties of these materials hinders their successful use for maxillofacial prosthetics.

This difficulty with polyurethanes after UV exposure prompted a screening of UV stabilizers to be used in polyurethane systems to make the materials suitable for maxillofacial prosthetic use. This screening of currently available UV stabilizers revealed that only a few performed satisfactorily.⁹ This lack of efficiency may be attributed partly to the inherent complicated nature of the polyurethane systems and partly to the lack of comprehensive and systematic research concerning the behavior of UV degradation of polyurethanes. In the present study, we also examined the effect of the few satisfactory UV stabilizers on the physical/mechanical properties of the polyurethane elastomers, particularly the aliphatic types, because, even though the physical appearance of the material remained unchanged, the mechanical properties could often deteriorate as a result of UV aging. A fully satisfactory UV stabilizer must be examined for changes in physical appearance as well as its influence on mechanical properties.

EXPERIMENTS

Materials

Calthane ND2300 (from Cal Polymer Co.),¹¹ the same polyurethane described in an earlier report,⁹ was used in the present study. It contains two components, A and B. Part A is an aliphatic diisocyanate-terminated prepolymer and part B is a hydroxy-terminated polyester. (The detailed chemical structure of Calthane ND2300 is not available due to a trade secret.) The UV absorbers selected for examination were Tinuvin 328 and Tinuvin 770 from Ciba-Geigy.¹² The chemical structure of Tinuvin 328, an amine-substituted benzotriazole, is shown below.



In rats, the LD_{50} of a single dose of Tinuvin 328 is greater than 5 g/kg.¹² This chemical, which is highly soluble in organic solvents and is compatible with our polyurethane system, is fully described by Ciba-Geigy.¹² Tinuvin 770, though still in the experimental stage, is apparently the best obtainable UV absorber since no tackiness and yellowing were observed in the polyurethane (i.e., Calthane ND2300) after a UV exposure of more than 500 hr.⁹ The manufacturer has not made public the chemical structure of Tinuvin 770; however, it is a sterically hindered amine-substituted benzotriazole.¹² An antioxidant, Irganox 1010, was also employed as it is highly compatible with polyurethane systems and is neither discoloring nor staining.¹² It is a high molecular weight symmetrical molecule with four sterically hindered phenolic hydroxy groups.

Processing, UV Aging, and Mechanical Property Measurement

The procedures used in the present study were the same as those in an earlier investigation.⁹ However, an RS-4 sunlamp from George W. Gates and Co. was used as a source of UV light rather than a carbon arc weatherometer, because the RS-4 sunlamp allowed the convenience of holding the samples in a horizontal position. According to ASTM D638-76a specification, the samples were cut in the dumbbell shape for tensile tests prior to the UV aging and to eliminate the difficulty of cutting a tacky film. The overall dimension of the dumbbell-shape testing specimen is 4.5 in. long and 0.75 in. wide. The length and width of the narrow section are 0.27 and 1.31 in., respectively. The thickness of the testing sample was 0.00284 in. Complete details of this test are given in ASTM D638-76a. The exposed tensile specimen was periodically removed from the UV source at predetermined times based on the results of an earlier report.⁹ When samples exhibited initial tackiness, they were removed from UV exposure.

Tensile measurements were subsequently determined by means of an Instron Tensile Testing Machine according to ASTM D638-76a with cross-head and recording chart speeds of 2 in./min and 1 in./min, respectively. The modulus of elasticity values determined from the stress-strain curves at strains of 100%. The elongation at break was also determined from the stress-strain curve.

RESULTS AND DISCUSSION

The deterioration of mechanical properties of the Calthane ND2300 polyurethane with and without UV stabilizers at various periods of UV exposure is summarized in Table I. The corresponding percentages of retention of these properties are shown in Figures 1, 2, and 3. System A contained no UV stabilizers; system B contained Tinuvin 328; a mixture of Tinuvin 328 and Irganox 1010 was incorporated into system C and Tinuvin 770 was added to system D.

The following general conclusions were reached: (1) The addition of UV stabilizers improves the resistance of those materials to harmful UV light. (2) The tensile strength and modulus of elasticity decreases with increasing UV exposure. The rate of decrease, however, is much less for the specimens with UV stabilizers. (3) The elongation at break shows the opposite effect; it increases with the increasing duration of UV aging. This phenomenon occurs in all systems, with or without the UV stabilizers. The aforementioned conclusions will be discussed individually in detail below.

The significant improvement of the UV stability of systems B, C, and D over that of system A suggests that the problem of UV aging of polyurethane elastomers could be partially solved by the incorporation of some specific UV stabilizers. The system without any UV stabilizer, as shown in system A, was degraded after 24 hr of UV aging. Systems B, C, and D still maintained their original tensile strength after this time period. The C and D systems displayed an even greater UV resistance than did the system that contained only Tinuvin 328 (system B). This difference in the efficiency of the UV stabilizers is shown in Figure 1, wherein the retention of properties is indicated according to the length of time the polyurethanes were exposed to UV and the kind of UV stabilizers used. After 290 hr of UV aging, the tensile strength of the C system was 65% of the unexposed system. The tensile strength of the D system retained 63% after 355 hr of UV exposure. The B system, however, lost 79% of its tensile strength after 120 hr of UV exposure and was degraded completely after 200 hr of UV aging. Therefore, the C and D systems are definitely superior to the B system and appear to be superior to the A system. The B system exhibited the greatest decrease of tensile strength between 48 and 120 hr. The significant decrease of tensile strength of the C system, however, was found between 170 and 290 hr. The D system was somewhat different as its tensile strength

TABLE I
The Effects of Different Kinds of UV Stabilizers on the Mechanical Properties of Calthane ND2300 Polyurethane Elastomer^a

UV Aging in Hours	Mechanical Properties		Tensile Strength, psi				Elongation at Break, %				100% Modulus of Elasticity			
			A		B		C		D		A		B	
	UV		A	B	C	D	A	B	C	D	A	B	C	D
0			465	465	465	465	360	360	360	360	155	155	155	155
6			285				590				60			
16			150				695				25			
24				410		460		405				125		140
48				350				435				100		
72					500	450			435	450		45	115	110
120				100										
170					425	285			440	480			95	55
290					310				455				70	
355						300				720			30	
800						partially degraded				partially degraded				partially degraded

^a The samples were formulated with a ratio of A/B = 3/2 and the concentration of UV stabilizer was 1.5% by weight; UV source—RS-4 sunlamp. A—no UV stabilizer; B—Tinuvin 328; C—Tinuvin 328 plus Irganox 1010; D—Tinuvin 770

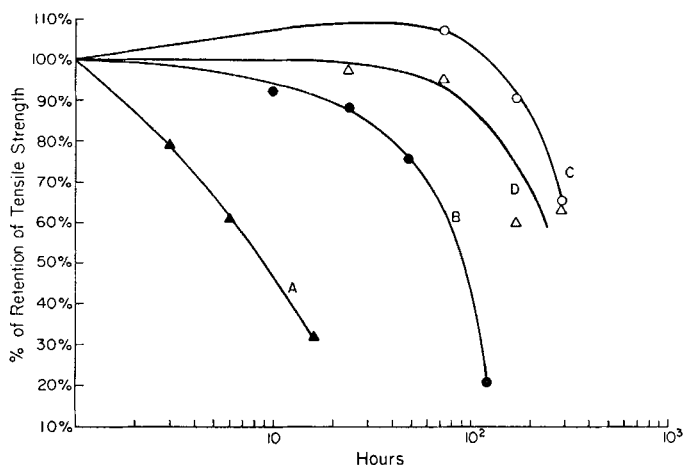


Fig. 1. The effect of different kinds of UV stabilizer on the tensile strength of Calthane ND 2300 polyurethane upon various durations of UV exposure. \blacktriangle , system A: no UV stabilizer; \bullet , system B: Tinuvin 328 only; \circ , system C: a mixture of Tinuvin 328 and Irganox 1010; \triangle , system D: Tinuvin 770 only.

degenerated markedly between 72 and 170 hr, but it displayed no further degeneration between 170 and 355 hr. The tensile strength was maintained at a virtually constant value of about 60%. Therefore, a summary of the systems in terms of tensile strength could be given as follows:

The B system degenerated most at a middle stage of UV exposure and exhibited a continuing degeneration of its properties with UV aging. The C and D systems degenerated most at a later stage of UV exposure and gradually lost their tensile properties over a period of time. Therefore, systems C and D are considered to be superior to the A and B systems.

The failure of the B system probably stemmed from its lack of suitable antioxidants. This speculation is supported by a comparison of the B and C systems. An addition of 0.75% by weight of an antioxidant would considerably improve the service life of system C. After 170 hr of UV exposure, the B system became partially fluid whereas the C system, with the same UV stabilizer plus an antioxidant, retains up to 91% of its tensile strength. The incorporation of an antioxidant in the system would block the occurrence of UV-initiated autoxidative degradation and hence protect the system better than the one without it. Autoxidation is common in poly(olefin)

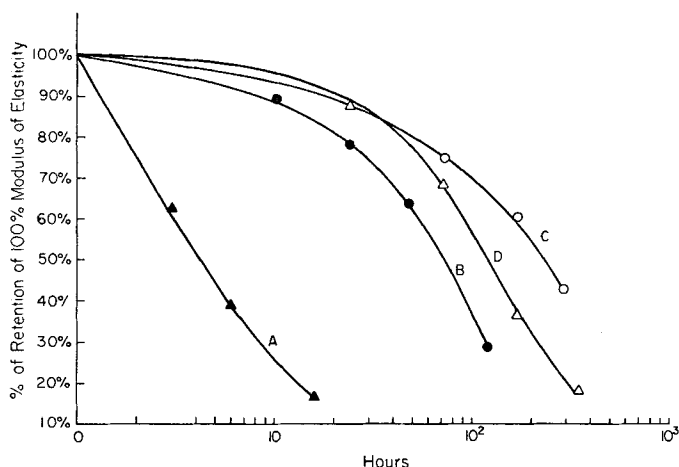


Fig. 2. The effect of different kinds of UV stabilizer on the modulus of elasticity of Calthane ND2300 polyurethane upon various durations of UV exposure. \blacktriangle , system A: no stabilizer; \bullet , system B: Tinuvin 238 only; \circ , system C: a mixture of Tinuvin 328 and Irganox 1010; \triangle , system D: Tinuvin 770 only.

materials,^{10,13} but is less known in polyurethane systems.^{7,8} The D system in which no antioxidant was added, however, shows the same degree of protection against UV light as the one with an antioxidant. Though it may appear contradictory to our earlier speculation, a careful scrutiny of the background information of Tinuvin 770 would provide us with an explanation of this contradiction. Tinuvin 770—as declared by the manufacturer, Ciba-Geigy—operates through dual antioxidant paths of peroxide decomposition and alkyl radical termination as well as through an energy quenching pathway. Hence, because of its unique chemical structure, Tinuvin 770 can function as an antioxidant as well as an UV absorber.

The failure of the C and D systems, subsequent to a long period of UV exposure, imposed some new problems in the systems that we are currently investigating. Even though the Tinuvin 770 and the combination of Tinuvin 328 and Irganox 1010 showed some promise in UV resistance, both allowed degeneration after a period of 800 hr and 355 hr, respectively. In addition, the physical appearance of the former system (Tinuvin 770) as reported earlier⁹ demonstrated that no tacky appearance was observed after 500 hr of UV exposure. This nontackiness could lead to the erroneous assumption that the Tinuvin

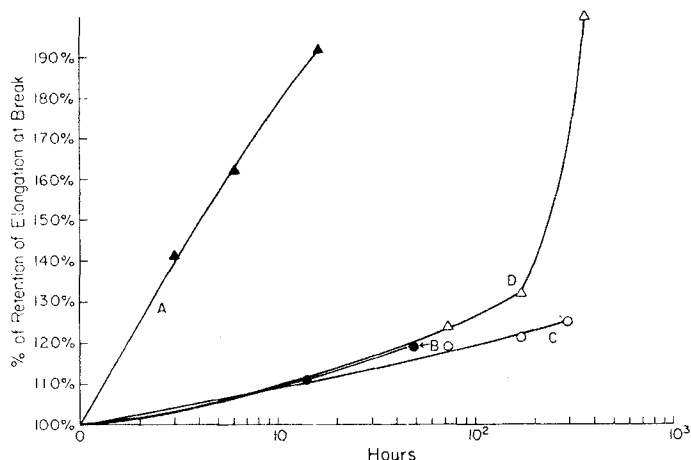


Fig. 3. The effect of different kinds of UV stabilizer on the elongation at break of Calthane ND2300 polyurethane upon various durations of UV exposure. \blacktriangle , system A: no UV stabilizer; \bullet , system B: Tinuvin 328 only; \circ , system C: a mixture of Tinuvin 328 and Irganox 1010; \triangle , system D: Tinuvin 770 only.

770 might be an excellent UV stabilizer for the Calthane ND2300 system. The unchanged physical appearance does not imply a lack of change in the physical and mechanical properties. Significant changes can be seen in Table I and Figures 1 and 2.

The increase of elongation at break that occurs after increased UV exposure, as shown in Figure 3, is also noteworthy. This increase occurs in all four systems regardless of whether UV stabilizers were present. The magnitude of increase in the A and D systems exceeded that in the B and C systems with most of the increase in the D system occurring after 170 hr of UV aging (67% increase from 170 to 255 hr). The B and C systems showed moderate increases, mainly in the early stage of UV exposure. For example, almost a 20% increase occurred within 72 hr exposure whereas only a 6% increase occurred between 72 and 290 hr in the C system.

Additional information relating to the UV degradation of polyurethane films can be further explored by comparing the stress-strain curves of unexposed and exposed samples. A typical result is shown in Figure 4 in which stress-strain curves of the unexposed sample A (no UV stabilizer), 170 hr UV exposed sample C (containing Tinuvin 328 and Irganox 1010), and sample D (containing Tinuvin 770 only) are shown. The stress-strain curves were similar for all three samples.

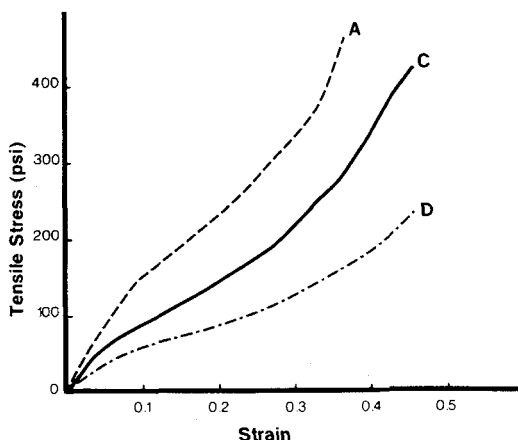


Fig. 4. The effect of UV aging on the stress-strain curves of Calthane ND2300 polyurethanes. A, unexposed sample containing no UV stabilizer; C, 170 hr UV exposed sample containing Tinuvin 328 and Irganox 1010; D, 170 hr UV exposed sample containing Tinuvin 770 alone.

However, UV exposure of samples C and D resulted in the reduction of their mechanical properties and rendered them more extendable than unexposed ones. The UV effect was most profound in the system containing Tinuvin 770 and is in accordance with Figures 1–3. At small strain, the UV effect was not pronounced whether the sample had UV stabilizers or not. At large strain, differences in mechanical properties of different UV stabilizers became significant. The variation in mechanical properties is a result of chain scission brought about by UV aging. Similar phenomenon had been observed in aromatic polyurethanes.^{14,15}

In summary, some UV stabilizers do prolong the service life of the system described, but they are not completely satisfactory. Physical appearance in conjunction with physical/mechanical property tests are necessary to ensure the efficiency of any UV stabilizer. A combination of a UV stabilizer and an antioxidant is the most satisfactory method of increasing the resistance of the materials to UV degradation.

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