

Tensile Strength of Polyurethane Exposed to Nitrogen Dioxide

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Synopsis

Polyurethane prepared from tetramethylene glycol and diisocyanate was exposed in the form of films to small pressures of NO_2 and to NO_2 plus air. Tensile strength was measured as a function of exposure time and temperature with an apparatus especially constructed for the purpose of measuring mechanical properties in different environmental "atmospheres."

EXPERIMENTAL

Film Preparation

The polymer originated from the same sample used previously for a study of chain scission and crosslinking due to NO_2 exposure.^{1,2} Films were cast from ca. 2.5% by weight solutions of the polymer in a 9:1 by volume mixture of phenol-water. The films were dried before exposure under vacuum for ca. 48 hr at 60°C and could be removed easily from the glass plates on which they had been cast. All films were 30 μ thick within 6%. The intrinsic viscosity of the polymer in the phenol-water mixture was $[\eta] = 1.1$ dl/g, its density was ca. 1.2 g/cm³, and its melting point was above 190°C.

Tensile Strength Apparatus

The apparatus is schematically depicted in Figure 1. It can be charged with NO_2 and other gases either alone or in conjunction with air, and the film can also be irradiated with near-ultraviolet light. The assembled apparatus is placed into a thermostated box kept constant within $\pm 0.5^\circ\text{C}$; temperatures above 0°C down to -50°C could be obtained in this box, which was located in a "walk-in" refrigerator kept at constant temperature within $\pm 1^\circ\text{C}$. The tensile apparatus glass container was connected via glass tubing to a large volume (ca. 21 liters) and eventually to a mercury diffusion pump backed by a rotary oil pump.

Loads were applied to the polymer films via a metal spring having a very small temperature coefficient (supplied by John Chatillon Inc., New York City). Extension of the spring could be measured by means of a cathetometer to 0.005 cm. The spring was activated by rotating the glass rod

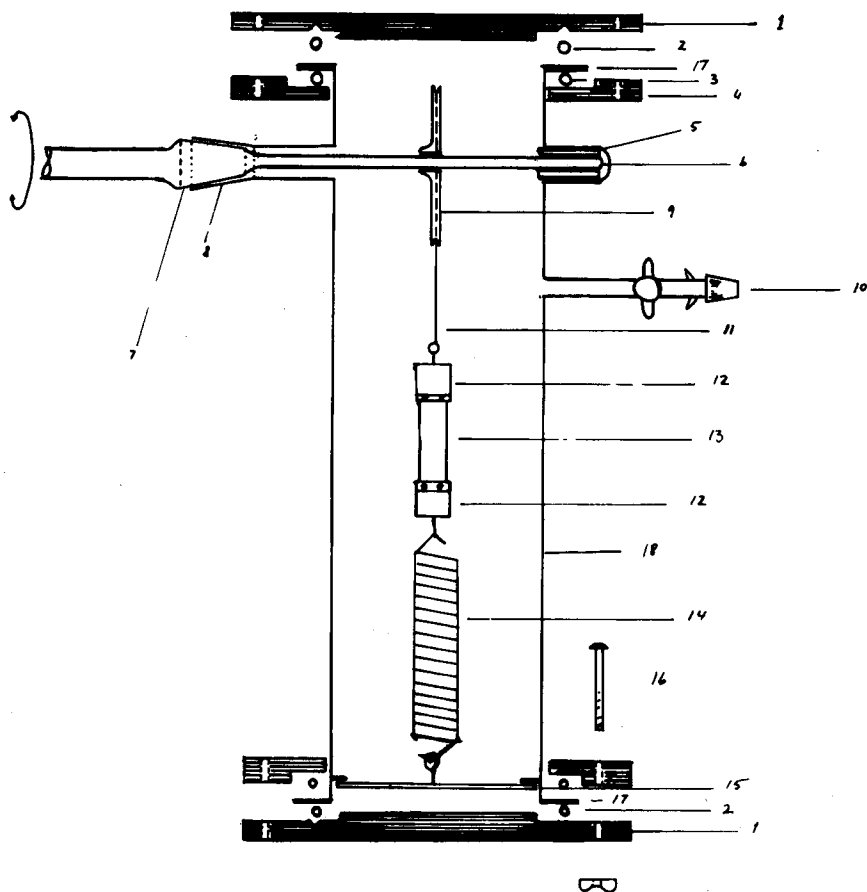


Fig. 1. Tensile strength apparatus: (1) lid (Al); (2) Teflon O-ring coated on both sides with Fluorolube GR-544; (3) Neoprene O-ring; (4) support (Al); (5) Teflon bearing; (6), (7) glass rod with male joint, Fluorolube GR-362 used at this joint; (9) aluminum wheel; (10) connection to high-vacuum line; (11) stainless steel piano wire (0.25 mm); (12) stainless steel clamps; (13) polyurethane film; (14) calibrated spring; (15) aluminum plate; (16) screws for tightening lids on both ends; (17) flat joint (flange); (18) glass body; (19) point observed with cathetometer.

(6,7) and thus winding the wire (11) on to the Al wheel (9). Rotation of the glass rod was effected by means of gear wheels located outside the thermostated box. Grease used for the joint of the glass rod was Hooker Fluorolube No. GR-544, and for low temperatures, GR-362 (below 0°C to -28°C). GR-544 was used for all other joints of the apparatus. This grease is not affected by NO_2 .

The spring was calibrated with weights over a range of 0 to 2500 g. Loads could be measured within 0.2 g. The temperature coefficient of the spring was found to be negligible (ca. $3.3 \times 10^{-2}\%$ per 1°C). An average force constant of 2.5×10^{-3} cm/g was taken for a range of temperatures from $+23.1$ to -33°C . The length of the unextended spring was 9.715 cm.

Method of Measurement

A film (3.5 cm \times 1.3 cm \times 0.003 cm) was clamped in such a way that the length of the free film was always 2.5 cm. This was achieved by locating the clamps in depressions made in a wooden board exactly 2.5 cm apart. Only the weights of the spring and one of the clamps (total 102 g) were exerted on the film before extension of the spring. The whole glass apparatus was then evacuated and the desired temperature was eventually established.

The requisite NO₂ pressure was obtained by keeping solid or liquid NO₂ at such a temperature that its vapor pressure equalled the pressure at which the film was to be exposed (e.g., 5 mm Hg of NO₂ at -45.5°C). The large volume assured that the NO₂ pressure remained constant during exposure. Actually, the whole apparatus was filled first with NO₂ except for the evacuated tensile apparatus container. After this container had reached the required temperature, NO₂ was also admitted to it. The pressure before opening this container had to be slightly higher (all volumes were known) than that of the desired one to allow for gas expansion. By this time, the NO₂ gas in the apparatus had been shut off from the NO₂ trap supplying the vapor pressure.

In case the experiment was carried out with NO₂ in 1 atm of air, the latter was dried and introduced into the apparatus after the NO₂ pressure had been established. Actually, the air pressure was ca. 7% lower than 1 atm due to expansion into the container, but this did not have any noticeable effect on the results.

The tensile strength of the polymer in air alone was 104 kg/cm² at 22°C. The film was exposed for the requisite time to NO₂ without a load being applied (except for the weight of the spring plus one clamp).

Loading of the spring was started ca. 30 sec before the end of the exposure time and was followed with the cathetometer until rupture occurred. Extension of the film from the start of loading to rupture was ca. 2 mm. The actual cross section at rupture was calculated.

Results

Tensile strength plotted versus exposure time to 5 mm Hg of NO₂ alone or with 1 atm of air, respectively, is shown in Figures 2 to 5. Tensile strength decreases with exposure time at any one temperature. The rate of decrease is appreciably faster if air is also present; whether this rate is constant, as indicated in Figure 5, cannot be decided at present.

The rate of decrease of tensile strength can be expressed by

$$-\frac{dS}{dt} = k(S - S_f) \quad (1)$$

or integrated

$$\ln \frac{S_0 - S_f}{S - S_f} = kt. \quad (2)$$

where S_0 , S_f , and S are the tensile strengths at $t = 0$, $t = \infty$, and t , respectively, and k is a rate constant.

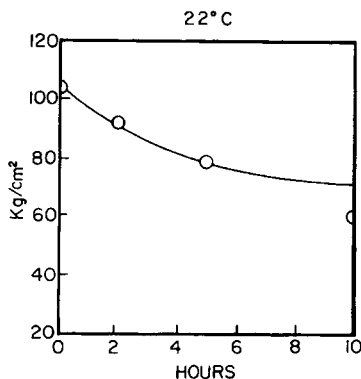


Fig. 2. Tensile strength vs. exposure time (5 mm Hg of NO_2) at 22°C.

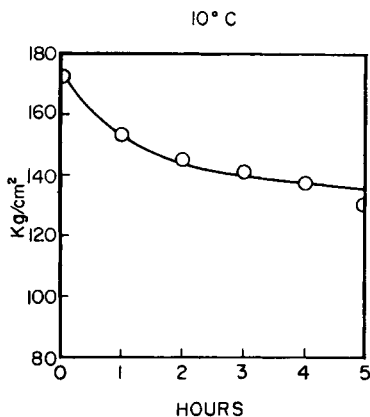


Fig. 3. Tensile strength vs. exposure time (5 mm Hg of NO_2) at 10°C.

In Figure 6, $-\ln[(S_0 - S_t)/(S - S_t)]$ is plotted versus t . The respective k values (in hr^{-1} , 5 mm Hg of NO_2) are as follows: 0.60 at -5°C , 0.75 at $+10^\circ\text{C}$; and 0.33 at $+22^\circ\text{C}$.

The tensile strengths plotted versus temperature for various exposure times pass through maxima near 10°C , which shifts slightly to higher temperatures with increasing exposure times (Fig. 7).

Several measurements were attempted at -22°C and 5 mm Hg of NO_2 ; however, after exposure for ca. 45 min, the films ruptured under the weight of the spring and clamp only.

The slope of the plot of tensile strength versus exposure time in air plus 5 mm Hg of NO_2 at 10°C amounts to $130 \text{ kg/cm}^2\text{-hr}$, whereas the corresponding initial slope for exposure at the same temperature to NO_2 alone is only $24 \text{ kg/cm}^2\text{-hr}$. If the film is kept longer than about 55 min exposed to NO_2 plus air at 10°C , it breaks before extension of the spring.

CONCLUSIONS

Decrease in tensile strength of the films on exposure to NO_2 is a direct consequence of chain scission due to NO_2 . It was ascertained in a pre-

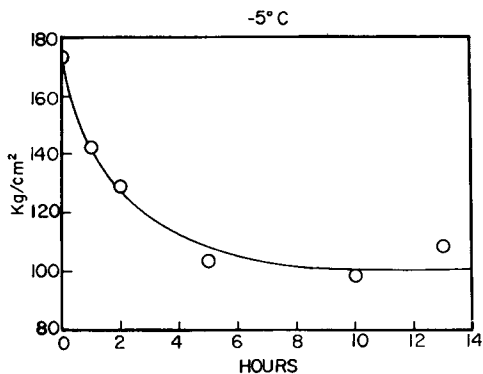


Fig. 4. Tensile strength vs. exposure time (5 mm Hg of NO₂) at -5°C.

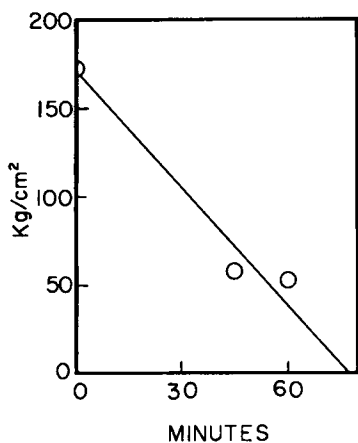


Fig. 5. Tensile strength vs. exposure time (5 mm Hg of NO₂ plus 1 atm. of air) at 10°C

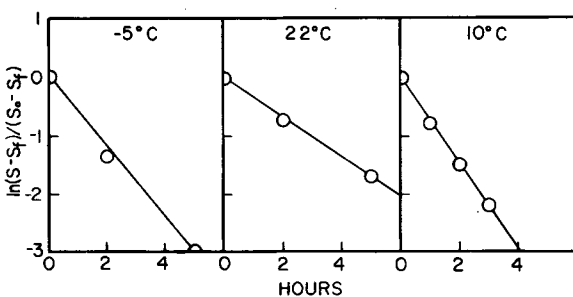


Fig. 6. Plot of $-\ln [(S_0 - S_x)/(S - S_x)]$ vs. exposure time for data in Figs. 2, 3, and 4.

vious study² that chain scission, crosslinking, CO₂ formation, and changes in IR spectra take place on exposure of such films to NO₂; this is accelerated by simultaneous presence of air. Mechanisms for these processes were presented in the previous paper. It appeared from the results of these studies that chain scission becomes predominant over crosslinking at lower temperatures; these processes were investigated over a temperature range

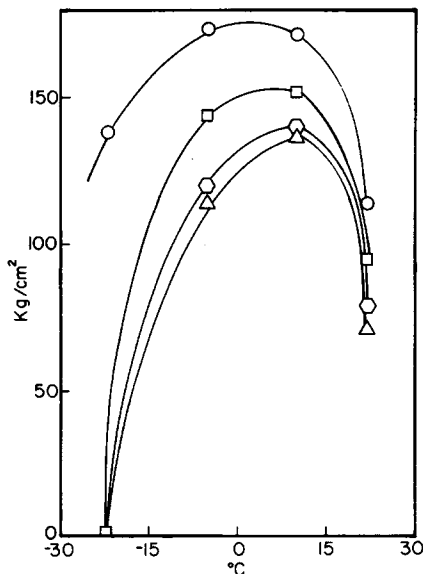


Fig. 7. Tensile strength vs. temperature at various exposure times (5 mm Hg of NO_2).

from 15°C to 60°C . This would account for the decrease in tensile strength on exposure to NO_2 found here.

The occurrence of maxima in the strength-temperature curves is probably due to complicated interactions of transition point, rate of load application, temperature of exposure, chain scission, and crosslinking. Chain scission and crosslinking were found to be diffusion controlled.²

SUMMARY

Tensile strengths of polyurethane films, prepared from tetramethylene glycol and diisocyanate and exposed to NO_2 (5 mm Hg) and NO_2 plus air, were measured as function of exposure time and temperature (-22°C to $+22^\circ\text{C}$). Tensile strength decreases with exposure time and passes through maxima near 10°C as a function of temperature for definite exposure times. The rate of decrease in tensile strength in the presence of NO_2 plus air is appreciably larger than in NO_2 alone. A tensile strength apparatus suitable for the study of polymers in different atmospheric environments and temperature ranges was constructed.

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