

# Surface Oxidation of Cis-Trans Polybutadiene

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## Synopsis

Uncrosslinked cis-trans polybutadiene films were prepared on ultraclean glass microscope slides by uniform dipping. The samples were stored in different environments prior to evaluation of surface oxidation by dynamic contact angle using the Wilhelmy plate method and by X-ray photoelectron spectroscopy (XPS). Storage conditions evaluated were: (1) laboratory air at 20°C and 30% relative humidity; (2) vacuum at 0.1 torr; (3) distilled water equilibrated with air; and (4) degassed distilled water. XPS and contact angle analysis indicate that samples exposed to air undergo significant surface oxidation within 8 h. Exposure of polybutadiene to air-equilibrated water results in slower oxidation. Samples stored in degassed water demonstrated less surface oxidation. Vacuum-stored samples demonstrated the least surface oxidation. Dynamic contact angle measurements demonstrated that receding contact angles are more sensitive to changes in surface oxidation than are advancing contact angles, as expected. Changes in surface wetting characteristics are readily observed after only 1 h in laboratory air, although XPS analysis does not show evidence of oxidation within 4 h of air storage.

## INTRODUCTION

It is well known that butadiene rubbers are susceptible to environmental oxidation by ozone and by thermal and photochemical methods.<sup>1-4</sup> To stabilize these materials, antioxidants of several different types are used.<sup>5</sup> Our interests in the biologic interaction of these polymers required a knowledge of the oxidative stability of additive-free polybutadiene under normal laboratory handling conditions. A recent study showed that the adhesion characteristics of polybutadiene films is dependent upon short exposures to air, indicating that surface oxidation takes place very rapidly.<sup>6</sup> In this report, the surface oxidation of cis-trans polybutadiene exposed to various laboratory handling conditions is measured by Wilhelmy plate dynamic advancing and receding water contact angles and by X-ray photoelectron spectroscopy.<sup>7</sup>

## EXPERIMENTAL

Uncrosslinked cis-trans polybutadiene was obtained from Aldrich Chemical Company, Lot #07. Proton nuclear magnetic resonance (NMR) spectra show the geometry of this polymer to be 39% 1,4-cis, 52% 1,4-trans, and 9% 1,2-configuration. Gel permeation chromatography (GPC) in tetrahydrofuran (THF) using narrow-molecular-weight-distribution polystyrene calibration standards produced the following molecular weights:  $\bar{M}_n = 6.95 \times 10^5$  and  $\bar{M}_w = 1.85 \times 10^6$ . The polymer was purified by dissolving in toluene, extraction with 5% aqueous sodium hydroxide, drying ( $\text{Na}_2\text{SO}_4$ ), and precipitation into 2-propanol.

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The polymer was stored as a 3% solution in toluene under argon until use. Polymer films were prepared by slow, uniform dipping of cleaned glass microscope coverslips and 10 mm  $\times$  9 mm  $\times$  1 mm glass samples. Film thicknesses produced by this procedure measured approximately 2  $\mu$ m. The films were dipped and dried in air, a procedure which takes normally 0.5 h, and then vacuum dried at 0.1 torr pressure for 24 h to assure removal of solvent. The 0.5-h air exposure is thus the background level for the oxidation study.

X-Ray photoelectron spectroscopy (XPS) was done with a Hewlett-Packard 5950B instrument using monochromatic Al  $K\alpha_{1,2}$  radiation (1487 eV) with 800 W power at the anode; the spectra were charge referenced to the C-1s alkyl binding energy at 284 eV. Photoelectron spectra were obtained utilizing ten scans over a 20-eV binding energy range. Oxidation was monitored by use of the oxygen-1s peak intensity and by attenuation of the  $\pi$ - $\pi^*$  carbon-1s shakeup satellite due to olefinic bonding<sup>7</sup> as well as from the chemical shift features of the carbon-1s photoelectron peak. The  $\pi$ - $\pi^*$  carbon signal is observed at +7 eV from the main alkyl carbon line at 284 eV. The mean free path of both the C-1s and the O-1s photoelectrons is approximately 60  $\text{\AA}$ .<sup>8</sup> As the Hewlett-Packard instrument used here has a sample geometry in which the detected electrons are in a path 38.5° from the surface plane, about 63% of the signal detected is from the topmost 40  $\text{\AA}$  of the sample.

### Wilhelmy Plate Technique

In our laboratory, two techniques have been extensively used for measuring contact angles on fully hydrated surfaces. One technique consists of measuring captive air and octane bubbles on inverted samples submerged in water. The polar and dispersion components of the surface energy of the fully hydrated surface<sup>9</sup> can be estimated by this method. Work by Smith<sup>10</sup> and others has demonstrated good correlation between biologic cell adhesion to surfaces and their captive air and octane contact angle measurements. The captive air and octane contact angle technique, while providing useful information concerning the interface energetics, is rather slow to perform and, under normal circumstances, only provides a measure of the polymer-water-air receding contact angle.<sup>9-12</sup>

Most polymers demonstrate both an advancing and receding stable contact angle. The difference between  $\theta$  advancing and  $\theta$  receding is defined as contact angle hysteresis. Many hypotheses have been presented to explain hysteresis.<sup>11</sup> Langmuir<sup>13</sup> suggested that hysteresis is due to the overturning of molecules as the liquid advances and recedes over the surface.

Since most polymer systems display some form of hysteresis, the more informative Wilhelmy plate technique has been employed in our laboratory for more careful surface evaluation. The technique is simple and requires only a modest investment in equipment. The requisite equipment is already available in most laboratories. For these studies, a standard mechanical testing device (Scotts SRE500 mechanical testing machine) is used to raise and lower a beaker of 2 $\times$  distilled water at controlled speeds of approximately 40 mm per minute. Situated above the container is a Cahn electrobalance (model RM-2) which supports the test sample on a fine thread. The balance system is mounted separately from the mechanical tester and is vibrationally isolated (see Fig. 1). The mechanical

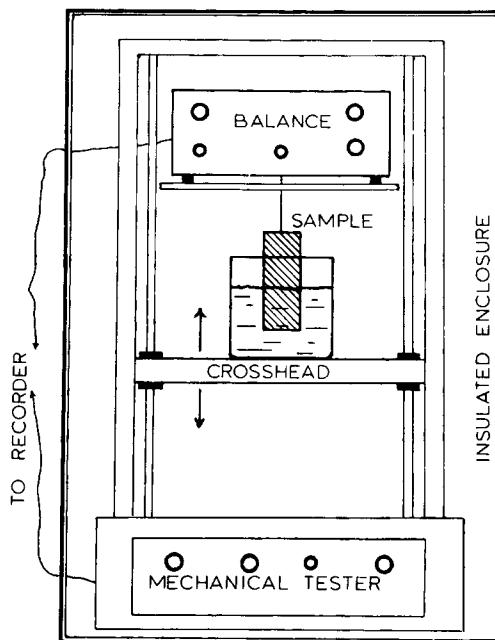


Fig. 1. Schematic of Wilhelmy plate equipment. A Scotts mechanical tester is used to raise and lower wetting liquid over sample interface at 40 mm/min. Wetting forces are measured on Cahn electrobalance. Equipment is entirely enclosed in temperature-controlled enclosure maintained at 20°C and 30% relative humidity.

tester and balance are contained in an insulated enclosure maintained at constant temperature (20°C) and humidity (30% RH). Various other systems for measuring the wetting force on the test plates have been used by other investigators,<sup>11-13</sup> including chain balances, strain gauges, and linear differential transformers. Electrical signals from the balance and crosshead travel are fed to an X-Y plotter to obtain the wetting curves [see Figs. 2(a), 2(b), and 2(c)]. Routine calibration of the electrobalance is readily performed by the addition of 100 or 200 mg tare weights. With the equipment described, a weight sensitivity of about 3.8 mg/mm is adequate for use with glass coverslips. For very small samples such as fibers and small tubing, a factor-of-10 more sensitivity is required.

As the crosshead is raised, the sample begins its immersion into the test fluid. When the sample first touches the fluid, a meniscus is formed and, as penetration of the sample into the liquid continues, the contact angle levels off, resulting in a constant slope on the X-Y recorder, which is a measure of the advancing angle. After some distance of immersion (2.5–3.0 cm), the process is reversed, the wetting liquid is lowered, and a constant measure of the receding angle is observed. Random vibrations resulting from the movement of the liquid over the sample surface lower the free energy barriers, allowing the advancing angle to more closely approach the maximum theoretical low-energy contact angle. Likewise, the receding angle more closely approaches the maximum high-energy surface contact angle.<sup>11</sup>

A typical curve for *cis-trans* polybutadiene is illustrated in Figure 2(a). The sample is immersed to a depth of about 2.5 cm (path 1) and then retracted. A second immersion is followed in path 2 that retraces exactly the advancing and

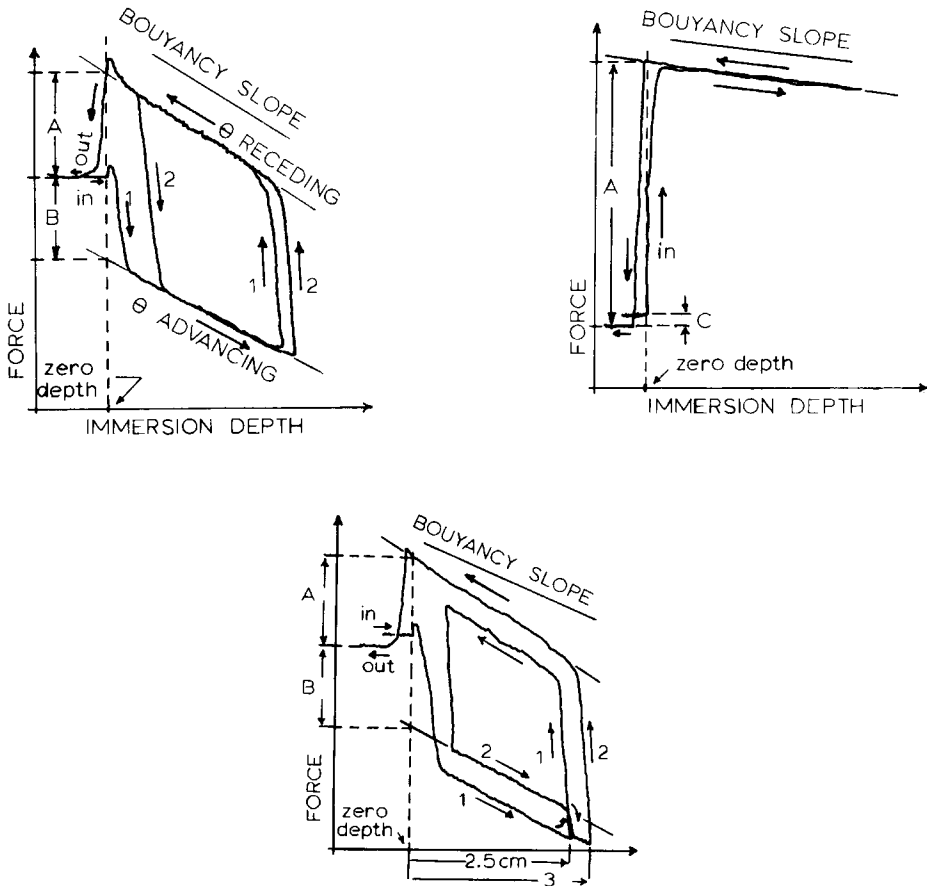


Fig. 2. (a) Typical Wilhelmy plate wetting curve of a polybutadiene sample. The buoyancy slope parallels both advancing and receding contact angles. The sample was taken through two successive dipping cycles to demonstrate reproducibility. Displacement A is used to compute the receding angle, while displacement B is used to compute the advancing angle. Curves are measured at the point of zero depth of immersion so the buoyancy effect can be neglected. (b) Wetting characteristics for hydrated, glow-discharged mica. The advancing curve is identical to the receding curve and parallel to the buoyancy slope. The slope is evaluated at zero depth of immersion. Note that the sample weight coming out of the wetting solution is less than the weight prior to the dipping point. The weight difference  $c$  is due to retained water droplets attached to the sample during hydration. Ultraclean, glow-discharged mica is assumed to be perfectly wetting and is used to measure the surface tension of wetting solutions. (c) Wetting curves of a nonhydrated hydrogel, poly(hydroxyethyl methacrylate). Due to the interaction of water with the nonequilibrated gel, the wetting curves do not parallel the buoyancy slope. Successive wetting cycles demonstrate increased wetting within seconds of a first immersion, demonstrating nonequilibrium.

receding curves in path 1. This indicates that no additional equilibration is taking place and that the water is not further interacting with the test sample. The buoyancy slope for the glass coverslip parallels the wetting curve.

Shown in Figure 2(b) are the wetting curves of radiofrequency glow-discharged (RFGD) mica. Freshly cleaved mica is extremely smooth, and, with a 2-min RFGD treatment in helium, it can be made perfectly wetting with no contact angle hysteresis. This also allows for accurate assessment of liquid surface tensions.

For simplification, straight-line approximations of the advancing and receding slopes are made and extrapolated to zero depths of immersion, and the buoyancy factor in eq. (1),  $V\rho g/p\gamma$ , can then be eliminated. Force A [Fig. 2(a)] is used to compute  $\theta$  advancing, and force B [Fig. 2(a)] is used to compute  $\theta$  receding. The basic equation is

$$\cos \theta = \frac{mg}{p\gamma} + \frac{V\rho g}{p\gamma} \quad (1)$$

where  $m$  is mass of the slide (g) as measured via electrobalance;  $g$  is local gravitational force (979.3 dyn/g);  $p$  is perimeter of sample (cm);  $\gamma$  is surface tension of wetting liquid; for water  $\gamma = 72.6$  dyn/cm at 20°C;  $V$  is volume of immersed sample at a particular depth; and  $\rho$  is density of wetting liquid. Zero depth of immersion is more readily observed as the sample first touches the water surface. When the sample is retracted from the water, a meniscus is carried above the water surface for some distance, depending upon the surface tension of the wetting liquid and the wetting characteristics of the sample.

In Figures 2(b) and 2(c), it is observed that the weight of the sample when withdrawn is not necessarily the same as when it is immersed, depending upon whether the sample is hydrated or nonhydrated. The initial weight and final weight may or may not be equal. For calculation purposes, the weight after sample retraction is used for measuring the force displacements. Measurements are frequently made with unequilibrated hydrogel systems, such as poly(hydroxyethyl methacrylate). Illustrated in Figure 2(c) are wetting curves of a nonequilibrated hydrogel surface. Note that the second path, yielding lower angles, does not retrace the first, because water is interacting with the gel surface and, because it interacts longer at the bottom than at the top, the buoyancy slope differs from the sample wetting slope. If the gel sample had been fully equilibrated, the first immersion path would look like Figure 2(a) and succeeding curves would be similar to Figure 2(b), showing no hysteresis.

It has been shown by Johnson et al.<sup>11</sup> that advancing angles are more reproducible on lower-energy (hydrophobic) surfaces, whereas receding angles are more reproducible on higher-energy (hydrophilic) surfaces. The dependence of advancing and receding angle measurements on the speed of immersion and withdrawal of the sample was also demonstrated. Speeds over 100 mm/min seem to influence the advancing angle more than the receding angle and are more noticeable on heterogeneous surfaces as compared to homogeneous surfaces. In general, better measurements are obtained with immersion and withdrawal speeds of less than 50 mm/min.

## Methods

Polymer solutions are prepared as 3 wt % solutions and filtered through 0.1- $\mu$ m filters into precleaned bottles. Ultraclean glass coverslips (Corning Glass), 24 mm by 60 mm, are slowly dipped into the polymer solution to coat both sides uniformly. These samples are air dried for approximately 0.5 h, followed by further drying for solvent removal in a vacuum desiccator (0.1 torr) at 20°C for 24 h. Following desiccation, samples are handled according to their specific protocol prior to measurement.

After 24 h of vacuum drying, the polybutadiene specimens were submitted

to each of the following environments: (1) laboratory air at 20°C and 30% relative humidity, (2) 2× distilled water equilibrated with air, (3) degassed distilled water, and (4) vacuum at 0.1 torr. Water was degassed by boiling and by argon purge. The water-soaked samples were stored in sealed polyethylene slide holders. For the degassed water-equilibrated samples, the slide holders were filled to eliminate any air pockets and then sealed. Samples were tested after exposure periods of 0, 4, 7, 24, and 92 h. For XPS analysis, water-soaked samples were dried for 2 h under vacuum before measurement. The air- and vacuum-stored samples were run immediately. All contact angles were measured immediately after the required time had elapsed. The hydration effect on contact angle is observable; after each measurement the samples were vacuum dried and remeasured dry. A slight increase in hydrophobicity was noted in the dried samples.

## RESULTS AND DISCUSSION

XPS analysis of the oxygen-1s, carbon-1s, and C-1s  $\pi$ - $\pi^*$  satellites shows that exposure to air for times greater than 4 h results in oxidation of the surface of polybutadiene. The air-equilibrated water environment resulted in a much lower rate of oxidation. The desiccator-stored samples showed the least degree of surface oxidation of the storage environments evaluated.

Representative carbon-1s spectra are given in Figure 3. Only the 4 and 24-h storage data are included for the vacuum [Fig. 3(a)], water [Fig. 3(b)], and air

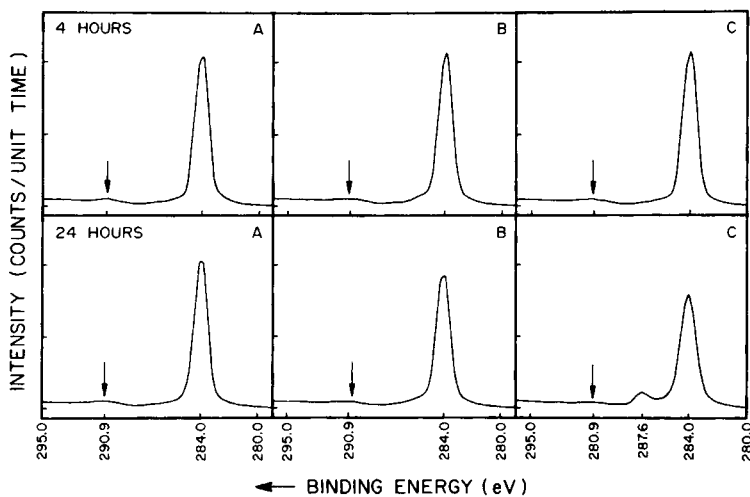


Fig. 3. Carbon-1s X-ray photoelectron spectra of *cis*-*trans* polybutadiene surfaces. (a) Samples stored in vacuum desiccator at 0.1 torr pressure, 20°C, for 4 h (top) and 24 h (bottom). (b) Samples stored in deionized/distilled water at 20°C for 4 h (top) and 24 h (bottom). (c) Samples stored in air in a laminar-flow, filtered air bench at 20°C, 30% RH for 4 h (top) and 24 h (bottom). Note the major C-1s peak located at 284.0 eV and the  $\pi$ - $\pi^*$  satellite peak at 290.9 eV. Air-stored samples develop significant surface oxidation at storage times exceeding 4 h. The 24-h air-stored sample (bottom right) shows the presence of an oxidized carbon peak at 287.6 eV (change of 3.6 eV), a characteristic feature for oxidized polybutadiene. The O-1s peak (not shown) analysis confirms the presence of oxidation. Minor differences in peak heights from panel to panel are not necessarily significant. Peak ratios and positions within individual panels are significant. Vertical scale bar represents 50,000 counts/channel.

[Fig. 3(c)] storage environments. The main C-1s line is charge-referenced to 284.0 eV. The  $\pi-\pi^*$  shake-up satellite is present at 6.9 eV higher binding energy (290.9 eV), as expected. No evidence of surface oxidation is present. Such evidence would be an asymmetry in the main C-1s peak resulting in a high binding energy tail or even distinct features. Such features are clearly evident in Figure 3(c), bottom, the 24-h air specimen. The peak at 3.6 eV from the main peak is characteristic of oxidized polybutadiene and could be due to a carbonyl-like carbon-oxygen state. A more detailed XPS study, including detailed analysis of the O-1s spectra, could provide more definitive information on the mechanism of oxidation.

The contact angle data shows comparable results (Fig. 4). The receding contact angle is more sensitive to surface oxidation than is the advancing angle. Both advancing and receding angles are quite stable to vacuum storage, indicating minimum oxidation under vacuum storage conditions. The oxidation of polybutadiene in air is rapid as noted by a decrease in the receding angle after the first hour, although 4 to 10 h of air storage are required before relatively large decreases in the advancing and receding angles (5 and 10° decreases, respectively) are noted. The water-soaked samples were measured as soon as their exposure time was finished. Hydration versus nonhydration of samples affects their contact angles, therefore, typically water-equilibrated materials which are not susceptible to oxidation still result in a decrease in contact angle.<sup>14</sup> To correct for this factor, a few samples were measured wet, then dried in vacuum and remeasured dry. Thus, water-N<sub>2</sub> equilibrated samples at 24 h measured 50° receding angle; after drying, the "dry" remeasured receding angle was 60°. These values correlate quite well with the XPS data which show that vacuum-stored samples undergo minimal or negligible oxidation, degassed water samples show greater oxidation, water equilibrated with air samples show next greatest oxidation, and air-exposed polybutadiene shows rapid surface oxidation. This rapid surface oxidation is also the conclusion derived from the polybutadiene adhesion study.<sup>6</sup>

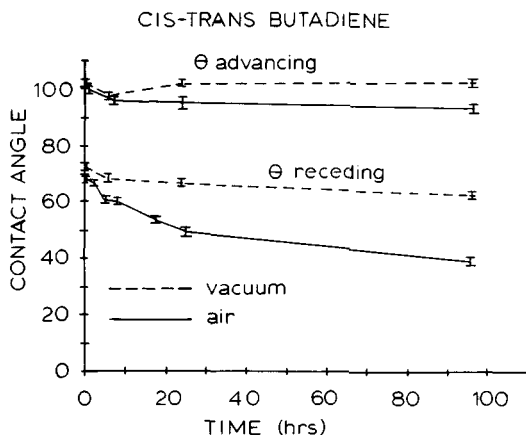


Fig. 4. Surface oxidation and related changes in wetting for cis-trans butadiene are readily apparent as storage conditions change. Wetting continues to change with time for all storage conditions except with vacuum storage. For clarity, only data for vacuum and air storage conditions are illustrated. Contact angle results of samples stored in degassed water and air-equilibrated water are similar to those stored in laboratory air.

These results should also be of significance to the study of butadiene-containing copolymers such as styrene-butadiene random copolymers and various styrene-butadiene di- and triblock copolymers. It is also important to note that the contact angle and XPS methods used are highly sensitive to surface modification and in particular to oxidation. Bulk analysis of such polymer films, such as by transmission infrared or even attenuated total reflectance infrared spectroscopy, would not be expected to show significant evidence of oxidation until much higher levels were reached. It is also important to note that these studies were performed on antioxidant-free material. The surface stability of antioxidant-containing material with respect to surface oxidation remains to be determined.

### CONCLUSIONS

Surface oxidation of cis-trans polybutadiene was determined using both advancing and receding dynamic contact angles as measured by the Wilhelmy plate technique and by X-ray photoelectron spectroscopy. The air-exposed surface undergoes rapid oxidation detectable by water contact angles within 1 to 4 h and by XPS after 4 h. Storage of samples under vacuum or in the absence of oxygen<sup>6</sup> essentially eliminates the surface oxidation. The Wilhelmy plate contact angle technique and X-ray photoelectron spectroscopy are useful tools for evaluating the surface characteristics of polymers. Antioxidant-free cis-trans polybutadiene can be stored under vacuum for up to 120 h without significant surface oxidation. Storage in oxygen-free water results in 2-3% surface oxidation after 24 h. Storage in oxygenated water or in air results in significant oxidation after 4 h.

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