UV Degradation of Polychloroprene Used in Waterski Boot Bindings

J. Fiedler, L. LaCasse, C. M. Liu, M. Muñiz, K. Reader
Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI

Statement of Problem

Neoprene has been used as binding boot material for over three decades, and is still widely used today. Due to the nature of the sport, equipment such as a ski is often left in the sun where UV radiation deteriorates the material until it loses its functionality. Figure 1 is an image of an orange waterski binding wrap that has degraded over many years. In the following experiment, the degradation of a similar wrap was investigated to determine the effects caused by UV radiation at a specific wavelength.

Figure 1: Digital image of a degraded neoprene wrap on a 1976 EP X2 slalom waterski.

Approach

UV Radiation

The solar spectrum includes radiation in the UV, visible light and infrared regions. Figure 2 shows the wavelengths and respective power intensity that reach the earth from sunrays. Polychloroprene tensile bars were placed in a 3D Systems Cure UV chamber for monochromatic UV exposure at a wavelength of 350 nm. According to ASTM G173-03,[1] the power intensity of the UV chamber was approximately 1 W*m^{-2}. The ratio of power intensity in the chamber to sunlight was found to be 10:1, so one hour in the UV chamber would be equal to ten hours in sunlight. The duration of UV exposure was varied, from 0 to 96 hours in 24 hour increments with six samples at each increment.

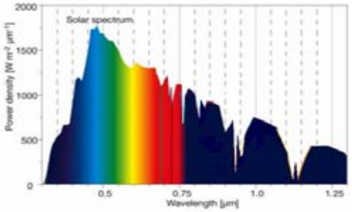


Figure 2: Spectrum showing energies of wavelengths produced by the sun.[2]

Testing

After UV exposure, tensile testing, Fourier transform infra-red (FTIR) analysis and SEM imaging were performed on each set of samples. Tensile testing was done using an Instron 4502 machine with a one kilogram load cell and an elongation rate of 500 mm/min following ASTM standard D412.[3]

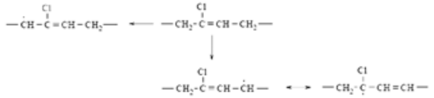
For FTIR, a Jasco FT/IR-4100 was used to obtain IR spectra to determine changes in the material's chemical structure. Jasco software was used to identify functional groups corresponding to peaks present.

After tensile testing, the failure surfaces of the tensile tested samples were coated with a layer of Au/Pd with a Hummer VI Sputtering System in preparation for SEM microscopy. The fracture surface of the as received and various UV-exposure time samples was then examined using a Philips XL SEM with electron beam energy of 7 keV. Images were obtained and recorded for further analysis.

Results & Discussion

Degradation Mechanism

Polychloroprene, like other polymers and elastomers, degrades when exposed to extreme heat and light conditions. The degradation mechanism of polychloroprene can be seen in Figure 3. The first step is hydrogen abstraction, which then leads to the production of one of three possible radicals as seen in Figure 3. This leads to the formation of conjugated double bonds which can be seen in Figure 4.[4] The cross-linking that occurs during this degradation is between the primary structural components of the rubber.[5] This indicates that instead of strengthening the material as is usually expected with cross-linking between polymer chains, the strength will decrease because the bonds between chains will become weaker.

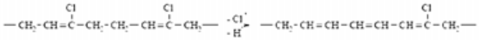


$$-\dot{C}H-\overset{Cl}{\overset{|}{C}}=CH-CH_2- \longleftarrow -CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2-$$

$$\downarrow$$

$$-CH_2-\overset{Cl}{\overset{|}{C}}=CH-\dot{C}H- \longleftrightarrow -CH_2-\overset{Cl}{\overset{|}{\dot{C}}}-CH=CH-$$

Figure 3: First step of the degradation of polychloroprene.[4]



$$-CH_2-CH=\overset{Cl}{\overset{|}{C}}-CH_2-CH_2-CH=\overset{Cl}{\overset{|}{C}}-CH_2- \xrightarrow[-H^{\cdot}]{-Cl^{\cdot}} -CH_2-CH=CH-CH=CH-CH=\overset{Cl}{\overset{|}{C}}-CH_2-$$

Figure 4: Conjugated double bonds of polychloroprene resulting from degradation.[4]

Tensile Tests

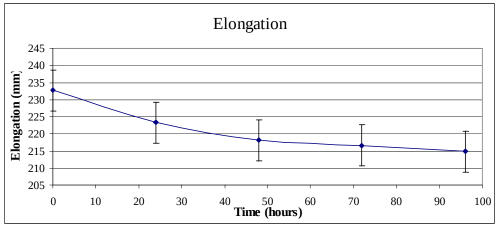


Figure 5: Elongation of samples with increasing duration of UV radiation.

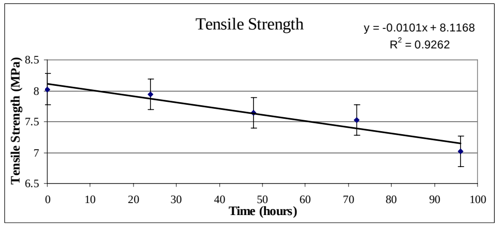


Figure 6: Tensile strength of samples with increasing duration of UV radiation.

Figures 5 and 6 show results from testing tensile bars exposed to UV radiation at 350 nm for different lengths of time. As shown in Figure 5, the elongation of the tensile bars decreased significantly with increasing duration of UV radiation. A similar trend is seen in Figure 6, where the tensile strength of polychloroprene specimens decreases with increasing radiation. An R^2 value of approximately 0.93 indicates that this degradation of tensile strength is linear. The degradation of tensile properties that is exhibited in Figures 5 and 6 is due to the increased cross-linking induced by UV radiation. As more cross-links form, the bonds between highly cross-linked sections become weakened and cause potential locations for failure. Therefore, increasing UV exposure causes additional cross-linking to occur and weakens the material in tension.

Fracture Surface Analysis

Figure 7 shows samples which were unexposed to UV radiation and 24 hours of radiation have smooth fracture surfaces in comparison to those which were exposed to 48, 72, and 96 hours of radiation. Differences are likely due to the degradation of the elastomer. The UV light excites bonds in the material, inducing the polychloroprene to form additional cross-linking bonds, causing the material to become more brittle. With increasing UV exposure (and increasing cross-linking), more crazing is seen from tensile testing. This is indicated in Figure 7d and 7e by red brackets. Each bump shows a section that has been cross-linked. The bonds between these highly cross-linked bumps are relatively weak, so they serve as points of failure. As failure propagates from each point, a plane is formed on the surface of the material. With more crazing points on different planes, the ridges that are indicated in Figure 7 by red arrows are formed.

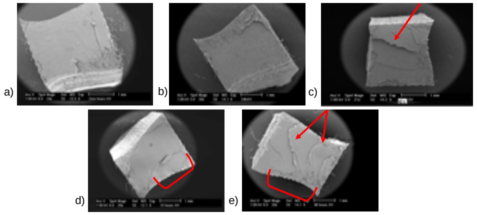


Figure 7: SEM images of the tensile fracture surfaces of the polychloroprene samples after UV radiation for a) 0 hrs, b) 24 hrs, c) 48 hrs, d) 72 hrs and e) 96 hrs.

FTIR

FTIR analysis was performed on as-received samples of polychloroprene, and on samples exposed to 24, 48, 72, and 96 hours of UV light. These results are shown below in Figure 8. The spectra show characteristic bands of polychloroprene, such as the C-H stretching band at ~2900 cm^{-1} and bending at ~1470 cm^{-1}, C=C band at 1660 cm^{-1}, and C-Cl band at ~825 cm^{-1}.

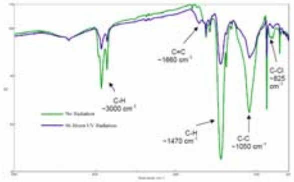


Figure 8: FTIR spectra for as received samples and samples exposed UV for varying times.

As the exposure time increased, the C-H, C-C, and C-Cl bands decreased while the C=C band increased.[6] The decrease in the C-H band was expected because of the process of degradation shown in Figures 3 and 4. It was not possible to determine from this analysis whether the C-H bending band or stretching band was primarily affected from exposure to UV light. From this analysis and current studies, it is unclear as to why the C-C and C-Cl bands decreased. The increased area of the C=C band attributed to the formation of carboxyl groups. It is difficult to interpret from this spectrum, but when the samples were exposed to UV light for a short amount of time, hydroxyl groups formed. These hydroxyl groups are unstable under UV exposure, and decomposed into the carboxyl groups that appeared in the spectrum at ~1660 cm^{-1}.

Conclusion

Polychloroprene degrades when exposed to UV radiation. Samples were exposed to UV light in various 24 hour increments. These UV and as received samples were subjected to tensile testing, SEM imaging of the fractured surfaces, and FTIR analysis. Tensile testing showed a continual decrease in strength with increasing exposure to UV light due to cross-linking. This occurs from free radicals formed during exposure. SEM images showed increased crazing and fracturing with increasing exposure. This was due to the decreasing tensile strength, which allowed for more breaking points in the material. FTIR analysis showed characteristic functional groups associated with polychloroprene. As UV exposure increased, the C-H, C-C, and C-Cl bands decreased while the C=C band increased. The decrease in the C-H band was expected because of the degradation mechanism of polychloroprene, and the increase in the C=C band occurred because hydroxyl groups decomposed into carboxyl groups.

Future

There are relatively few studies performed on the UV degradation of polychloroprene. There is much additional work that can be done in this area to approach the complete characterization of the degradation behavior of polychloroprene rubber for waterski binding applications. The following are suggestions for further research of this issue:

1. Testing the effects of the entire solar spectrum
2. Testing the effects of both high and low temperature
3. Testing the effects of lubricants such as dish soap, Newt Juice, etc.
4. Fatigue testing to simulate the use of the material several times a day

Acknowledgments

We would like to thank Eddie Roberts at HO Sports, Keith McIntyre, Justin Scanlon, Professor John Halloran and Chang-Jun Bae. The gracious and generous help of these people made this experiment possible.

References

1. ASTM G173-03. "Standard Tables for Reference Solar Spectral Irradiances: Diret Normal and Hemispherical on 37° Tilted Surface". ASTM International. 2006.
2. "Solar Cell Materials- production and features." http://www.pvresources.com/images/technologies_pic02.jpg.
3. ASTM D412-98a(2002)e1. "Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension". ASTM International. 2002.
4. Handbook of Material Weathering, 3rd Ed., 2003, pp 446-447.
5. Kazhdan *et al.* "A study of Structure Formation in the Degradation of vulcanized Rubbers." L.Ya Karpov Physicochemical Institute. 1965.
6. Freitas, A.R., Vidotti, G.J., Rubira, A.F., Muniz, E.C. "Polychloroprene degradation by a Photo-Fenton process." Polymer Degradation and Stability 87. Pg 425-432. October 2004.