

Chemorheological Studies on the Environmental Susceptibility of a Model System for Adhesives and Sealants

K. T. Tan[†], D. J. Benatti, C. C. White and D.L. Hunston
Building and Fire Research Laboratory, National Institute of Standards and Technology
100 Bureau Dr., Stop 8615, Gaithersburg, MD 20899-8615

[†]To whom all correspondence should be addressed: kar.tan@nist.gov

Introduction

The susceptibility of adhesives and sealants to hostile environments has been a concern for many years. Extensive efforts have been made to examine the effect of spectral ultraviolet (UV) radiation, temperature and humidity on the durability of adhesives and sealants (see for example [1]). To expand their applications and to increase service life of the materials, understanding the mechanisms of environmental attack is crucial. The objectives of the present research therefore are threefold: (a) to establish the mechanisms of environmental attack on a model adhesive and sealant system exposed to laboratory accelerated environments, (b) to investigate the effect of mechanical stress/strain on the mechanisms of environmental attack, and (c) to establish a correlation between field exposure and laboratory accelerated exposure. A linear triblock copolymer based upon styrene-butadiene-styrene (SBS) was selected as the model system because (a) the SBS copolymer is the precursor for adhesives and sealants, and (b) the inherent susceptibility to degradation of the unsaturation in the polybutadiene mid-block provides a rapid means to establish chemorheological changes of the model system. This paper presents results from the first objective of this research.

Experimental

Materials

Styrene-butadiene-styrene (SBS) triblock copolymer used in the present work was KRATON D1101k[‡] supplied by KRATON Polymers. The mass percentage of styrene is 31 %. The composition of the butadiene matrix consists of 42 % of *trans*-1, 4-butadiene, 49 % of *cis*-1, 4-butadiene and 9 % of 1, 2-vinyl-butadiene [2]. Specimens were prepared from solution casting using a solution mixture of 80 % by mass of toluene and 20 % by mass of KRATON D1101k.

Fourier-transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectroscopies

FTIR and UV-vis specimens were prepared by spin-coating technique. Coatings were applied to calcium fluoride disks and spun cast at 105 rad s⁻¹ for 20 s. The coated disks were cured at 50 °C for an hour in a nitrogen gas blanket. FTIR analysis was undertaken using a Nexus 670 Spectrometer in transmission-absorption mode. The spectra were collected over a range of 650 cm⁻¹ to 4000 cm⁻¹. UV-vis analysis was undertaken using a Perkin-Elmer Lambda 900 Spectrometer.

Dynamic mechanical thermal analysis (DMTA)

DMTA specimens were prepared using a drawdown method. The solvent was slowly removed at 50 °C for two hours in a nitrogen gas blanket. The measurements were undertaken using a TA Instrument in tension mode. Dynamic temperature sweep measurements were made at a frequency of 1 Hz and a temperature range from -100 °C to 120 °C with a heating rate of 2 °C min⁻¹. The test specimens used were rectangular specimens with dimension of 10 mm x 5 mm x 0.4 mm.

Laboratory environmental exposure

The specimens were exposed to 30 °C at 0 % relative humidity using NIST integrating sphere weathering devices. A full description of the weathering device is given elsewhere [3]. The integrating sphere provides a source of collimated ultraviolet radiation in the 290 nm to 400 nm region of the spectrum and allows precise control of temperature and humidity. Five replicates were made for the FTIR and UV-vis analyses, whilst two replicates were made for the DMTA measurements.

Results and Discussion

Chemical property changes upon exposure

Subtraction of the initial spectrum before exposure from the spectra recorded after various exposure times reveals several interesting features (see Figure 1). It can be seen that broad absorption bands corresponding to oxidation products, i.e. hydroxyl functional groups at 3200 cm⁻¹ to 3600 cm⁻¹ and carbonyl functional groups at 1600 cm⁻¹ to 1800 cm⁻¹, increase with increasing exposure time. It has been established that the mechanism of oxidation of 1, 4-butadiene involves primary radical attack on the methylene group in the α -position relative to the double bond [4-5]; whilst the mechanism of oxidation in 1, 2-vinyl-butadiene occurs at the γ -position [6]. Subsequent oxygen addition and hydrogen abstraction results in the formation of unsaturated hydroperoxides, which are detected on FTIR spectra at 3400 cm⁻¹. The hydroperoxides are thermal and photo-unstable, and undergo homolysis to produce alkoxy radicals. Thermal-oxidation and photo-oxidation of the resulting alkoxy radicals lead to

[‡] Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedure. On no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

secondary hydroxyl and carboxyl functional groups (detected at 3200 cm^{-1} to 3600 cm^{-1} and 1600 cm^{-1} to 1800 cm^{-1} , respectively). It is noteworthy that the intensities of the hydroxyl and carbonyl functional groups reach limiting values after 10 days of exposure (see Figure 2). It has been suggested that the oxidative cross-linking reactions result in a decrease of the oxygen permeability of the material, which essentially impedes further oxidative degradation [5].

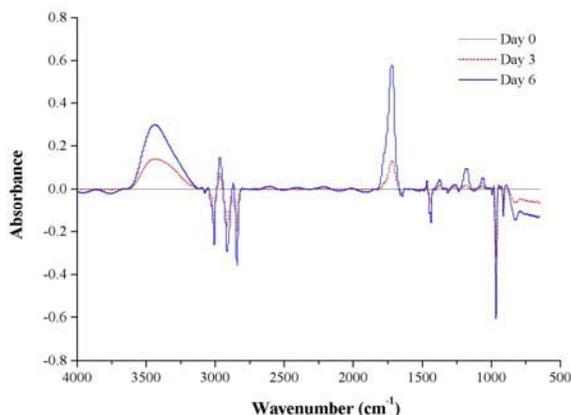


Figure 1. Transmission FTIR difference spectra between the initial unexposed specimens and the exposed specimens for two different exposure times (only spectra for two exposure times are shown for clarity of the graph).

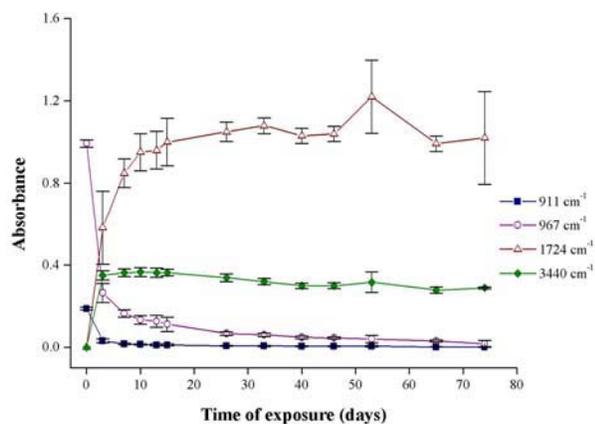


Figure 2. Kinetic evolution of the oxidation products and the consumption of the unsaturations during the course of experiments.

The intensities of the absorption peaks associated with the 1, 2-vinyl unsaturation of polybutadiene (911 cm^{-1} , 995 cm^{-1} , 1640 cm^{-1} , 2988 cm^{-1} and 3075 cm^{-1}) and the 1, 4 unsaturation of polybutadiene (967 cm^{-1} , 1438 cm^{-1} , 1652 cm^{-1} and 3005 cm^{-1}) are decreasing. In addition, there is a linear relationship between the intensity loss of absorption peaks at 911 cm^{-1} and 967 cm^{-1} , which are assigned to the out-of-plane bending of CH_2 in the 1, 2-vinyl unsaturation and the out-of-plane bending of CH in the *trans*-1, 4 unsaturation, respectively [7]. This observation suggests that the loss of the CH groups in the vinyl and *trans*-1, 4 unsaturations is closely related. After

10 days of exposure, the absorption peaks are no longer apparent. The loss of the CH and C=C absorptions may be attributed to cross-linking and saturation reactions occurring simultaneously [6]. It can be seen from Figure 1 that there is no significant change in absorption peaks related to phenyl functional groups (699 cm^{-1} , 750 cm^{-1} and 1609 cm^{-1}) and skeletal stretching of styrene (1190 cm^{-1}). Therefore, the styrene units do not play a role in the loss of the material within the time-scale of the experiments.

The exposed specimens exhibited a considerable yellowing with degradation, indicating the creation of visible light absorbing chromophores attributable to the butadiene unit [9]. The yellowness index is measured in accordance with ASTM D1925-70 [8] and the evolution of yellowness index as a function of exposure time is depicted in Figure 3.

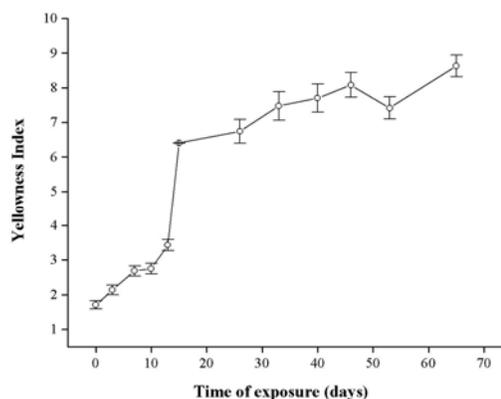


Figure 3. Evolution of yellowness index of the exposed specimens for various exposure times.

Mechanical property changes upon exposure

From the FTIR analysis, it is observed that the thermal and photo-degradations lead to formation of hydroxyl and carbonyl functional groups. Butadienyl radicals, created during the course of the oxidation process, attack the double bonds leading to cross-linking reactions [10]. Figure 4 shows the variation of the storage modulus as a function of temperature for different exposure time. The influence of cross-linking in the butadiene unit is evident from the increase in the storage modulus of the exposed specimens (see Figures 4 and 5). The oxidative cross-linking reduces the polymer molecular chain mobility and decrease free volume. Indeed, as may be seen from the $\tan \delta$ versus temperature curves as a function of exposure time (see Figure 6), a drastic decrease in the peak of $\tan \delta$ is observed. This is an indication of the extent of mobility of the macromolecular chain segments decreases with increasing exposure time [11]. The glass transition temperature for the butadiene unit increases with increasing exposure time, as is evident from the shifting of the $\tan \delta$ peak to higher temperature (see Figure 6). Such increase in T_g indicates a reduction in segmental mobility as the network tightens due to oxidative

cross-linking reactions.

During the early stage of exposure, the abrupt transition between the glassy phase and the rubbery phase of the butadiene unit implies that the butadiene and styrene units are phase-separated (see Figure 4). However, as the exposure time increases, the transitions are less distinctive, suggesting that the specimens become more heterogeneous. This is attributed to complex oxygen diffusion and chemical transformation in the material during the oxidation, which results in the creation of heterogeneity as a function of thickness of the specimens [6]. Also, as remarked earlier the styrene unit has been found not to play any role in the mechanism of degradation. Such hypothesis is further supported by the DMTA result, where the glass transition temperature of the styrene unit remains at 95 °C during the time-scale of the experiment.

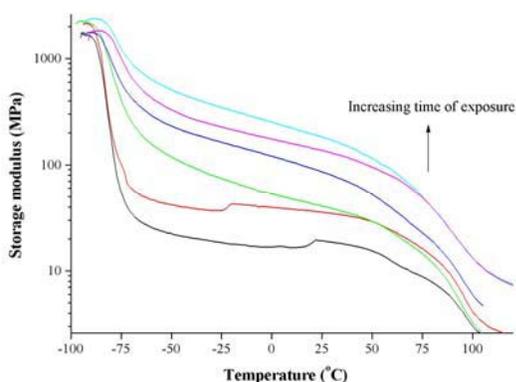


Figure 4. Storage modulus versus temperature for different exposure times.

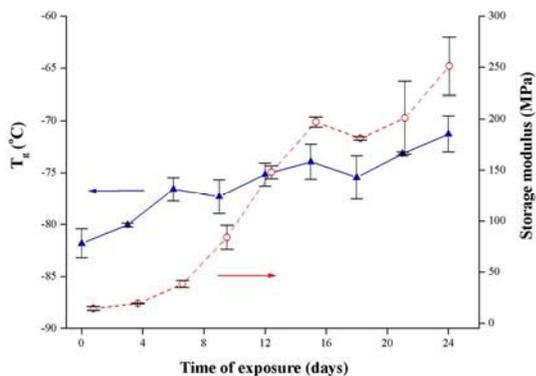


Figure 5. Evolution of storage modulus at 20 °C and glass transition temperature of the butadiene units for different exposure times.

Conclusions

The degradation of styrene-butadiene-styrene triblock copolymer has been characterized using DMTA, FTIR-transmission and UV-vis spectroscopies. From FTIR analysis, it is evident that the oxidative degradation leads to the formation of hydroxyl and carbonyl products. The degradation process proceeds by end-chain scission and cross-linking reactions in the butadiene unit of the exposed specimens. Such oxidative cross-linking reactions

render the specimens brittle, causing it to lose its desired mechanical properties. Indeed, an increase in the storage modulus of the specimens, as well as an increase in the transition temperature of the butadiene unit, have been observed using DMTA. Chemical property changes are highly correlated with mechanical property changes as the specimens degrade.

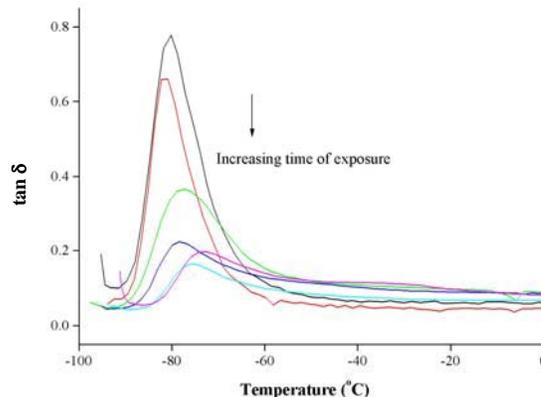


Figure 6. Loss $\tan \delta$ versus temperature plot for different exposure times.

Acknowledgements

The authors would like to thank Dr. Xiaohong Gu, Dr. Jon Martin and Dr. Tinh Nguyen of Building and Fire Research Laboratory, National Institute of Standards and Technology for valuable discussions. Also, KRATON Polymers is gratefully acknowledged for supplying the study material.

References

1. C.C White, K.T. Tan, E.P. O'Brien and D.L. Hunston, *Proc. Adhesion Soc.*, 2006.
2. E. Pedemonte, G. Dondero and G.C. Alfonso, *Polymer*, **16**, pp. 531-537, 1975.
3. J. Martin, J.W. Chin, W.E. Byrd, E.J. Embree and K.M. Kraft, *Polym. Degrad. Stab.*, **63**, pp. 297-304, 1999.
4. M. Piton and A. Rivaton, *Polym. Degrad. Stab.*, **53**, pp. 343-359, 1996.
5. C. Adam, J. Lacoste and J. Lemaire, *Polym. Degrad. Stab.*, **26**, pp. 269-284, 1989.
6. S.W. Beavan and D. Phillips, *Rubber Chem. Tech.*, **48**, pp. 692-704, 1975.
7. R.A. Dickie, R.O. Carter, J.S. Hammond, J.L. Parsons and J.S. Holubka, *Ind. Eng. Chem. Prod. Res. Dev.*, **23** (2), pp. 297-300, 1984.
8. ASTM D1925-70, 1988.
9. R.S. Salman and N.D. Al-Shama'a, *Polym. Plast. Tech. Eng.*, **30**(4), pp. 343-349, 1991.
10. K. McCreey and H. Keskkula, *Polymer*, **20**, pp. 1155-1159, 1979.
11. L.E. Nielsen and R.F. Landel, *Mechanical Properties of Polymers and Composites*, Marcel Dekker Inc., New York, 1994.