

Chemical and bonding effects of exposing uncured PBI-NBR insulation to ambient conditions

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ABSTRACT: Uncured Polybenzimidazole-Nitrile Butadiene Rubber (PBI-NBR) insulation experiences altered chemical and bonding phenomena if exposed to ambient conditions while in a sheet-stock configuration. Multiple lots of a PBI-NBR formulation exposed to ambient and slightly elevated temperature (100°F) conditions experience bonding degradation when vulcanized to a metal substrate. Chemical analyses show that tallow amine (clay particle surfactant) accumulates at the surface of uncured NBR as a function of ambient and 100°F exposure time. Additionally, thin film analyses suggest surface oxidation of NBR polymers when exposed to the ambient environment. Mechanical and chemical observations imply a correlation between vulcanized bonding performance with tallow amine diffusion and polymer surface reaction. The diffusion and reactivity of chemical species found in the PBI-NBR formulation has implications to other fields employing these components. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42636.

KEYWORDS: adhesives; ageing; rubber

Received 27 April 2015; accepted 17 June 2015

DOI: 10.1002/app.42636

INTRODUCTION

Following fabrication and cure of a NASA demonstration motor insulated center aft segment, bond verification witness panels were tested to assess the quality of the insulated segment. The insulation-to-case bond witness panel exhibited areas of low peel strength and insulation-to-adhesive failure modes. Further investigation indicated thin film insulation failure. The segment was dispositioned “reject and refurbish” and an investigation of the cause and appropriate corrective actions was initiated. Well into this investigation, resources were allocated to dissect the discrepant insulated segment prior to refurbishment. This dissection revealed insulation-to-adhesive failure modes similar to those seen on the bond witness panel. Additionally, bond testing revealed a previously unknown sensitivity: open and prolonged exposure of PBI-NBR surfaces prior to cure resulted in reduced bond capability. This exposure results in reduced bond strength and a change in failure mode from cohesive (failure within the insulation) to adhesive and thin film failures.

Tallow amine and NBR are both employed in a range of industrial, commercial, and private uses. NBR is a common polymer used in fuel hoses, gaskets, O-rings, gloves, and other areas.^{1,2} As with many rubbers, NBR is also used for insulation purposes.¹ Among the many uses of tallow amines, some of the most common are as surfactants, such as in textiles and fungicides, and as dispersants to aid in the dissolution/emulsification of solid constituents in polymeric mixes.³ In PBI-NBR, tallow

amine is used as the surfactant for an organo-montmorillonite nanoclay ingredient, which facilitates NBR polymer intercalation between the clay platelets. Extensive research on the preparation and structural benefits of NBR nanoclay reinforcement has been performed^{4–11} and the effect on cure characteristics has been documented.¹² Surfactant treated clays have also been used as an anti-tack release agent on uncured rubber.¹³ To date, research into the effects of tallow amine surfactant on NBR vulcanized bonding to metal substrates has not been explored.

The positively charged head group combined with the hydrophobic lipid chains found on quaternary tallow amines makes them ideally suited surfactants, emulsifiers, dispersants, and release agents, where interaction with two different mediums or surfaces is required. The amphiphilic nature (having hydrophilic and hydrophobic properties) of quaternary tallow amines makes them a key ingredient in fabric softeners where the amine head group binds to charged fibers, leaving the fatty acid tallow chains directed away from the clothing surface, giving it a soft, slick feel.¹⁴

EXPERIMENTAL

Ambient testing was accomplished by exposing uncured pads of PBI-NBR to a maximum of 20%RH environment at 68°F for a period of 71 days. Complementary mechanical and chemical tests were both employed to provide a comprehensive understanding of exposing uncured rubber. Traditional mechanical

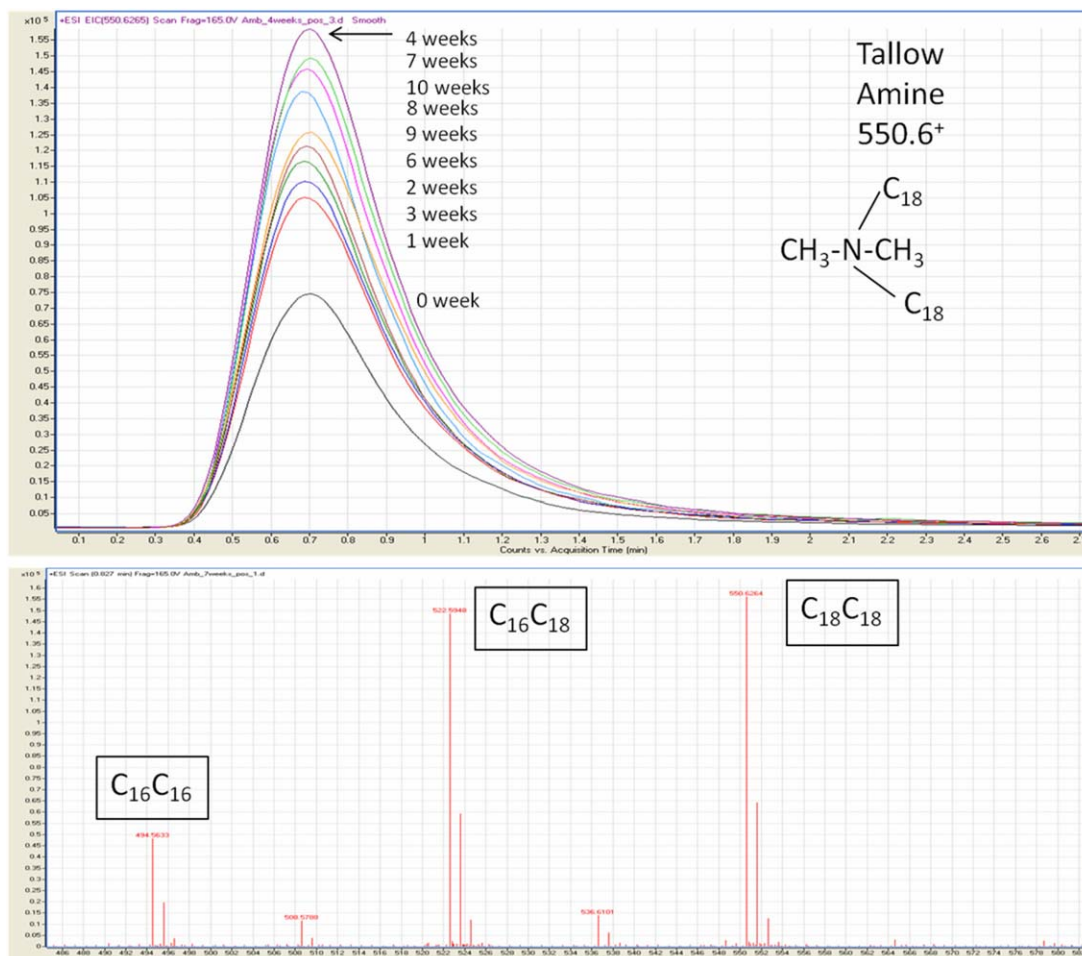


Figure 1. (Top) Extracted ion chromatogram overlays of tallow amine, m/z 550.63⁺, from hexane surface rinses of PBI-NBR exposed for 0–10 weeks under ambient conditions. (Bottom) Mass spectra of surface rinse indicating the most abundant tallow amine signals. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and chemical methodologies were utilized, along with MALDI MS, which has gained increasing application for polymer analysis over the past two decades.¹⁵ Elevated temperature testing was also performed in a low humidity environment with pads conditioned at 100°F for a period of 14 days. The base level of tallow amine was constant for all rubber pads tested. Throughout conditioning, samples were periodically removed from their respective environments and subjected to High Performance Liquid Chromatography/Mass Spectroscopy (HPLC/MS) analysis to identify surface chemical composition. During the same sampling period, conditioned rubber was used to fabricate vulcanized bond performance specimens. Follow-on Matrix Assisted Laser Desorption Ionization (MALDI) testing was performed on thin film NBR polymer mixtures in an attempt to characterize changes in polymer chemistry associated with the ambient exposure.

High Performance Liquid Chromatography/Mass Spectroscopy

All samples were prepared and analyzed under similar conditions and parameters. Each 8-inch by 8.25-inch uncured PBI-NBR sheet was uniformly rinsed with 4 or 9 mL of hexane.

Rinses were transferred to 20 mL scintillation vials and diluted to equal volumes. To prevent possible sublimation of the more volatile species, sample rinses were not dried down and reconstituted at equal concentrations prior to analysis. Samples were diluted 1 : 100 in Tetrahydrofuran (THF) or THF : H₂O (80 : 20) and analyzed in duplicate with LC/MS using a column-free injection on a HP 1100 HPLC, in series with an Agilent 6220 Time-of-Flight Mass Spectrometer (TOF-MS). A quaternary tallow amine standard was used at 0.001 mg/mL for single-point calibration. Sample injections of 5.0 μ L were eluted with an isocratic mobile phase of 80 : 20 THF : H₂O (5 mM NH₄Ac) at 0.25 mL/min. Stainless steel tubing was used for more uniform elution of amines. Within the Electrospray Ionization (ESI) source, drying gas was 11 mL/min at 250°C, with 3.5 kV capillary voltage. Residue masses, obtained by drying down the rinses after aliquots for LC/MS injection had been taken, were used to normalize the integrated ion counts.

Matrix Assisted Laser Desorption Ionization

Three polymer mixtures were generated with different components found in the PBI-NBR formulation. With the exception of stearic acid in mixture #1, the component–component ratio

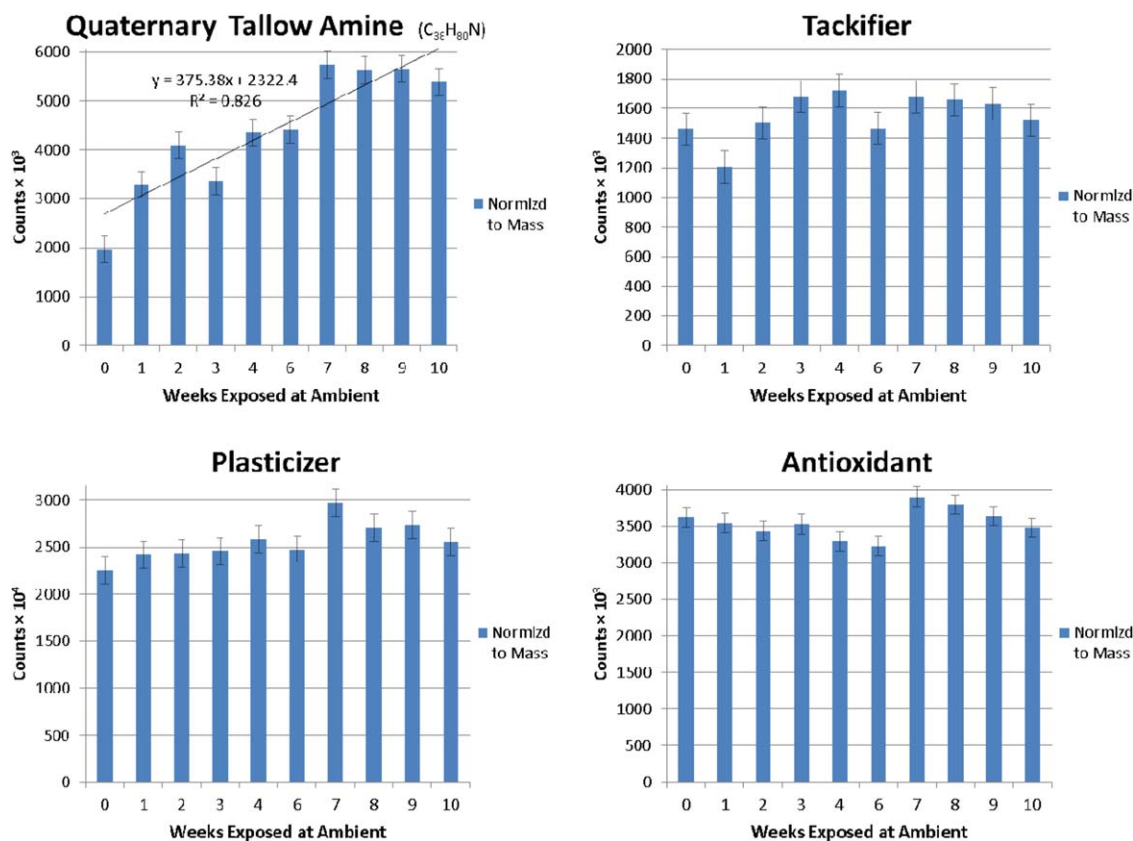


Figure 2. Normalized counts of the indicated species from ambient exposed, uncured, PBI-NBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

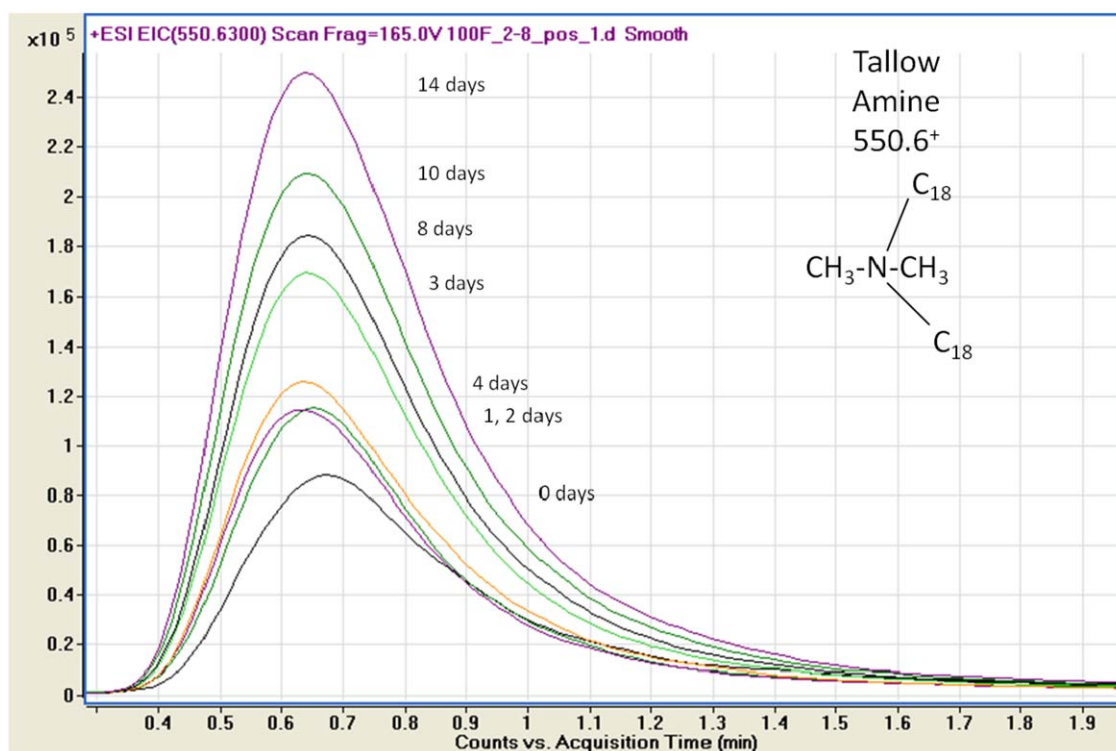


Figure 3. EIC overlays of quaternary tallow amine from the 100°F PBI-NBR hexane rinses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

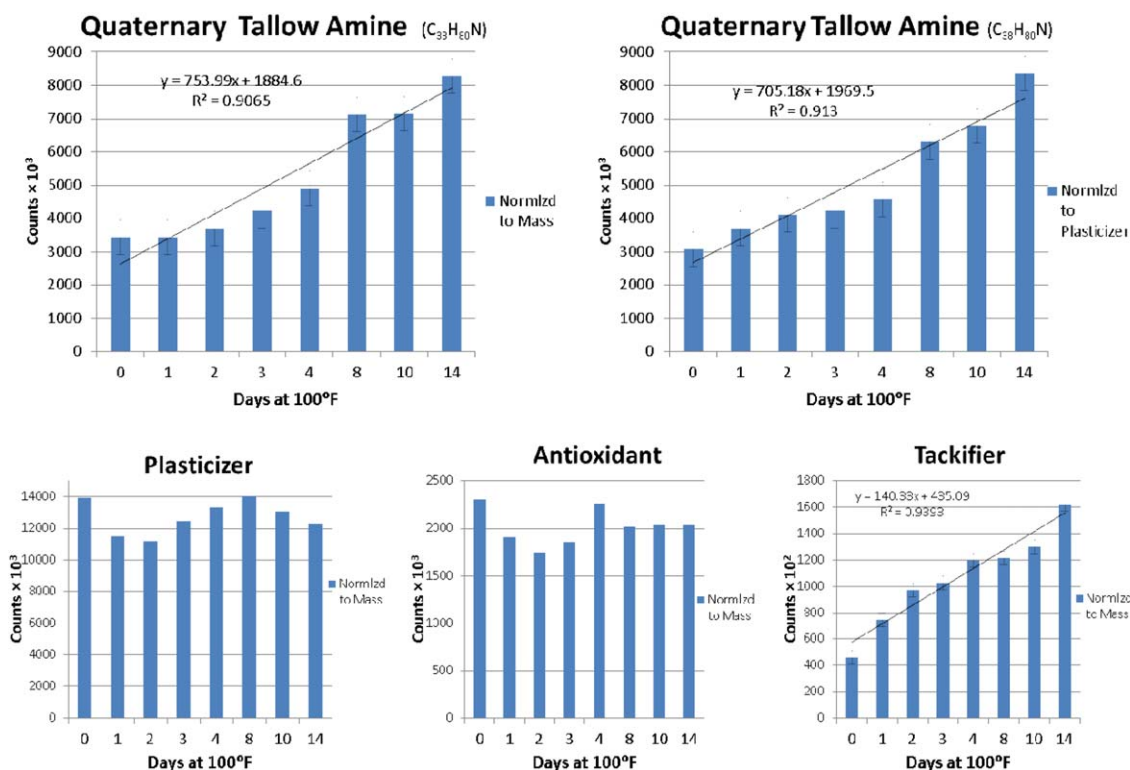


Figure 4. Quaternary tallow amine and other signal levels from 100°F PBI-NBR hexane surface rinses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in each mixture was kept approximately constant—equal to the ratios of the standard formulation. Three mixtures were made. Mixture #1 contained only the polymer constituents and stearic acid, while mixture #2 contained all components of the PBI-NBR formulation. Mixture #3 contained the polymer, nanoclay, plasticizer, tackifier, and antioxidant. Mixtures were solubilized in THF then spread as thin films with foam sponges onto pre-weighed 6-inch diameter watch glasses and allowed to dry. After drying, the watch glasses were weighed again to get the polymer film mass. Using a density of 1.2 g/cm³, film thicknesses were estimated at 5–10 microns. After 30 days of ambient exposure, films were solubilized in THF and prepared at 5 mg/mL.

Samples were prepared and analyzed analogously. All samples were prepared by stepwise deposition of salt, matrix, and sample solutions onto stainless steel plates. Approximately 1 μL Cu(NO₃)₂ in THF was deposited onto the stainless steel plate first, followed by 1.5 μL fresh retinoic acid matrix and 0.5 μL of polymer solution in THF. A Waters® Synapt MALDI-TOF/MS instrument was used for analysis. Typical parameters were employed. A 15-minute programmed scan using a 10 Hz, 3 ns pulsed nitrogen laser at ~20 to 25 μJ/pulse was used to ablate the target samples. Trap pressures were held at approximately 3.3×10^{-3} mbarr with 0.2 mL/min trap gas flow. The ion mobility function was not used. Calibration was performed prior to analysis with a Polyethylene Glycol (PEG) standard up to 4000 Da.

Bond Performance

Bond tests were conducted to evaluate the PBI-NBR-to-casebond adhesive strength at ambient laboratory temperature

(approximately 72°F). Tensile buttons were pulled at a rate of 0.50 inch/minute; peel tabs were pulled at an angle 90 degrees to the panel surface at 2.0 inches/minute.

RESULTS AND DISCUSSION

High Performance Liquid Chromatography/Mass Spectroscopy

Quaternary tallow amine signals measured increasingly abundant from surface rinses of uncured PBI-NBR, proportionate to the length of ambient and 100°F environmental exposure. Extracted Ion Chromatograms (EIC), representing total, un-normalized, integrated tallow amine signals from each PBI-NBR surface rinse, are seen in Figure 1. The quaternary species shown in Figure 1 was the strongest tallow amine molecular ion signal measured. A similar response was observed from the second-most abundant quaternary amine at m/z 522.60⁺ (not shown), which has an identical structure as that shown in Figure 1 except with two less hydrocarbons on one chain. A positive-ion mass spectrum of a PBI-NBR surface rinse, labeling the strongest tallow amine signals, is also shown in Figure 1.

The overlays shown in Figure 1 correspond to the absolute signal from each PBI-NBR sample. Mentioned above, samples were prepared at equal volume but not equal concentration. Therefore, the absolute signals were normalized to residue mass to account for discrepancies in sample preparation. Normalized signal levels are illustrated in Figure 2.

Shown in Figure 2 above, only the quaternary tallow amine exhibited a significant signal increase relative to ambient

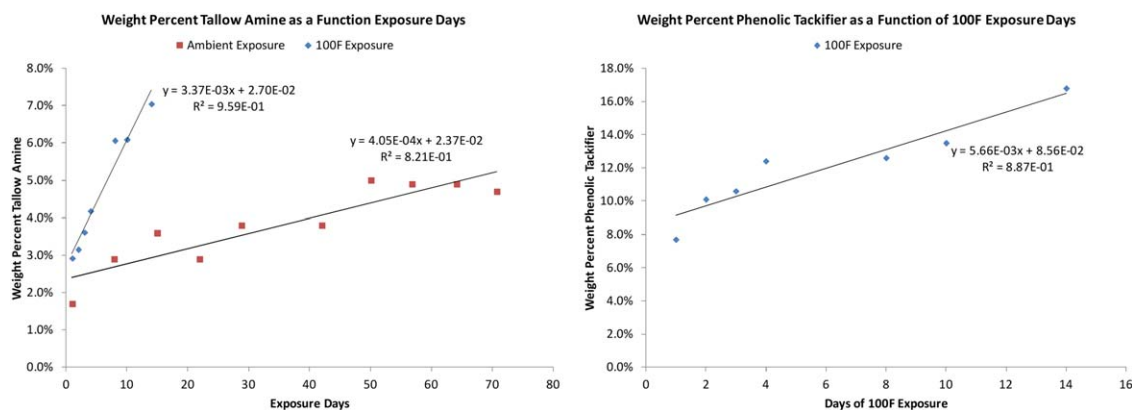


Figure 5. Tallow amine (a) and phenolic tackifier (b) weight percent as a function of exposure duration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exposure time. The trend of increased surface tallow amine is most pronounced when compared to the zero time rinse from either the absolute or normalized signals.

For PBI-NBR exposed to 100°F, the increased quaternary tallow amine from the surface rinses relative to exposure time was even more pronounced than at ambient temperature. As seen in Figure 3, absolute quaternary tallow amine signal is greatest for samples conditioned at 100°F the longest. Significant discrepancies in tallow amine concentration are observed between the zero time sample and those exposed at 100°F for several days—as compared to weeks for ambient exposure. This enhanced

difference is attributed to the thermodynamic driving force, separating the charged head group of the quaternary tallow amine from the hydrophobic rubber bulk. Therefore, accumulation at the rubber surface suggests that the amphiphilic nature of the quaternary tallow amine causes the charged, hydrophilic head groups to orient towards the air interface while the hydrophobic tail groups interact with the rubber. With the exception of $t = 3$ days, tallow amine signal increased linearly with time. Shown in Figure 3 and the corresponding plots of Figure 4, the tallow amine increase relative to exposure time is evident whether normalized or absolute.

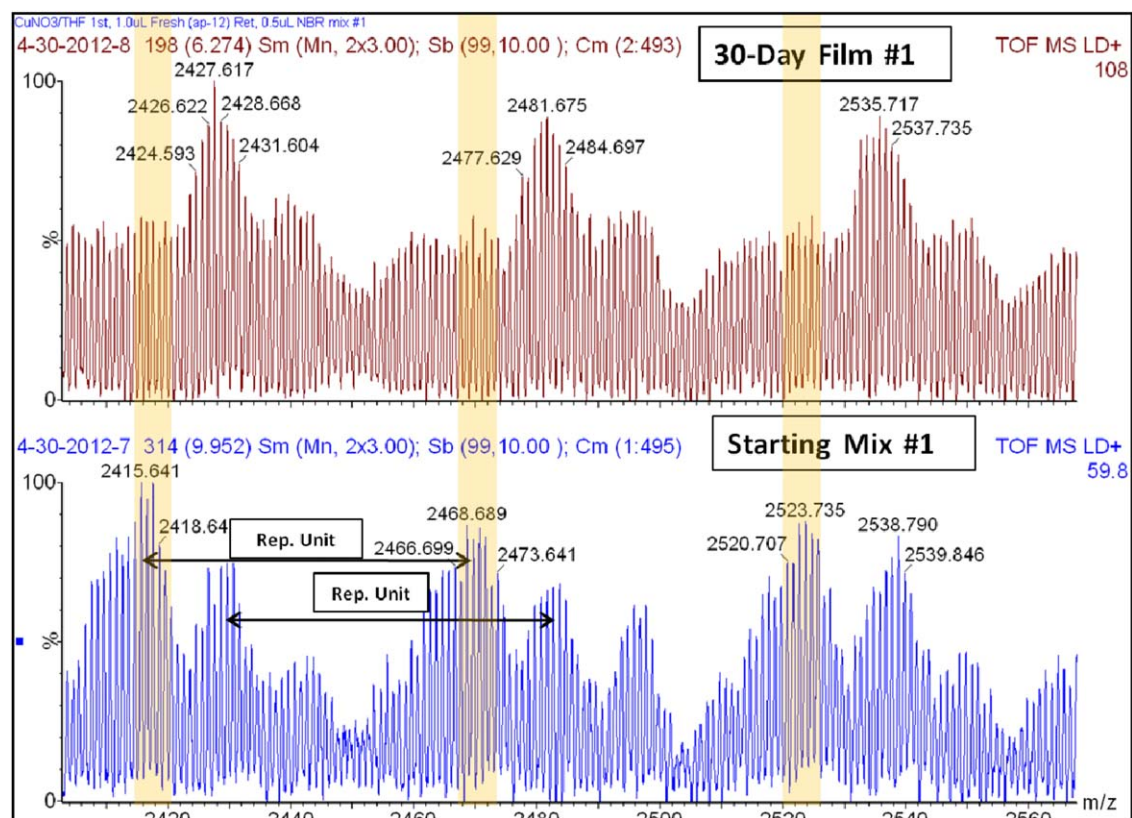


Figure 6. Positive MALDI mass spectra of mix/film #1 demonstrating the loss of the primary polymer peak (highlighted) after 30 days of ambient exposure of the film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

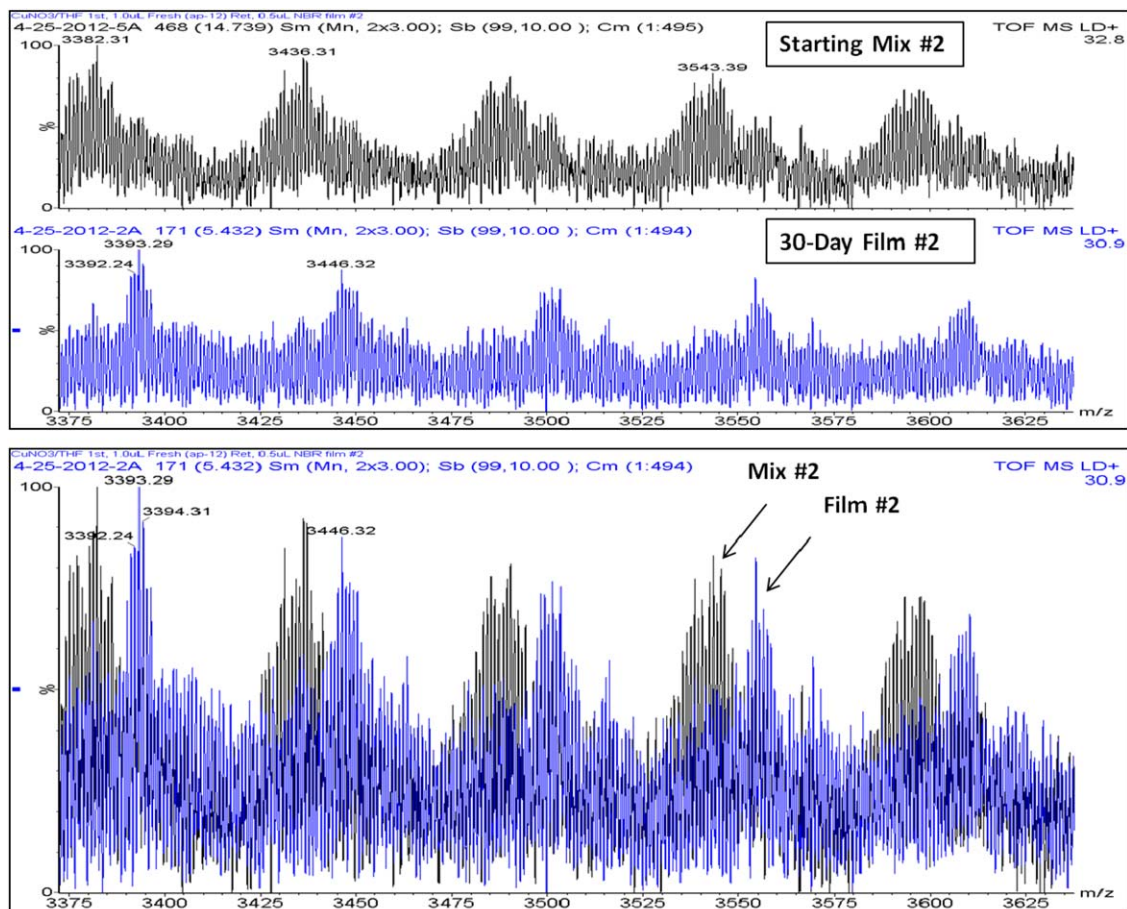


Figure 7. MALDI mass spectra of mix/film #2 again demonstrating polymer signal differences. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Shown in Figure 4, the formulation tackifier also exhibited increased surface accumulation with time exposed at 100°F. Increased tackifier may have acted to amplify the unbond at 100°F, but did not exhibit the same relative increase under ambient conditions.

As seen in Figures 3 and 4, normalization of tallow amine to residue mass or the formulation plasticizer both facilitate approximately linear responses with respect to number of days exposure at 100°F. To further illustrate surface accumulation with ambient and 100°F exposure, a plot of quaternary tallow

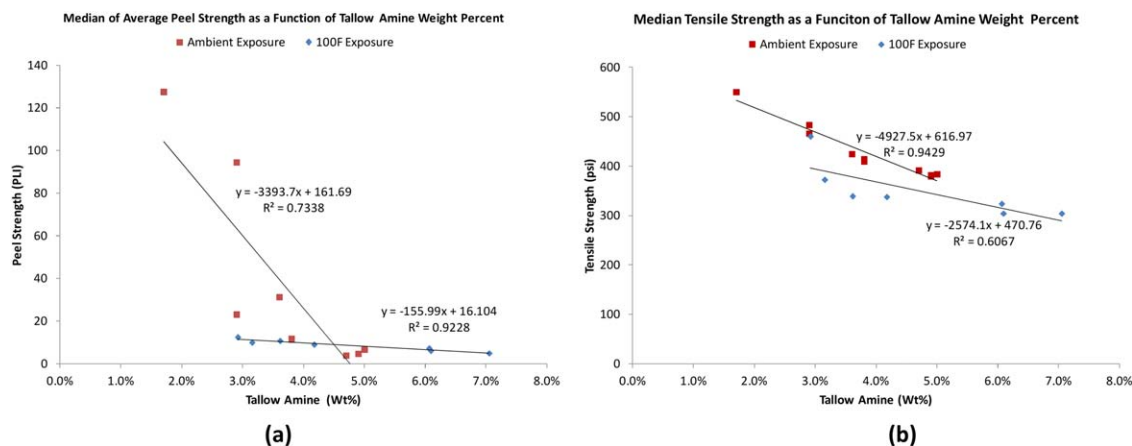


Figure 8. (a) Median peel strength and (b) tensile strength as a function of tallow amine concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

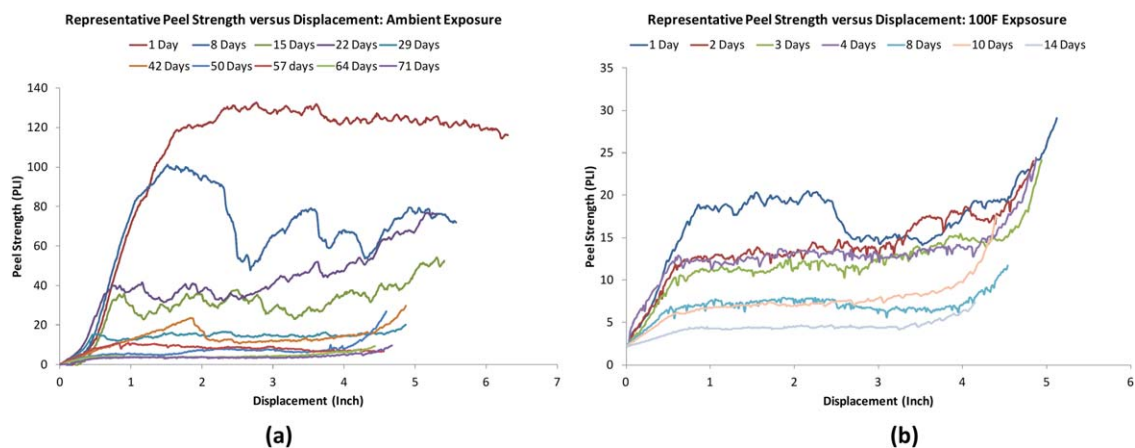


Figure 9. (a) Ambient and (b) 100°F exposure peel load traces as a function of exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amine concentration as weight percent of surface residue is given in Figure 5. Weight percent tackifier of total surface residue with 100°F exposure is also plotted in Figure 5.

Matrix Assisted Laser Desorption Ionization

Apart from the small molecules, MALDI-TOF/MS was used to measure possible changes in the NBR polymer upon prolonged ambient exposure. As detailed in the experimental section, thin films of the NBR polymers, mixed with other additives at formulation ratios, were exposed to ambient conditions and then analyzed with MALDI to determine possible changes in the polymer. While peak area differences in the Nipol polymer can be measured with Gel Permeation Chromatography (GPC), exact mass chemical changes in polymers were observed using MALDI-TOF/MS. Because MALDI is capable of taking exact mass measurements, distinct polymer reactions were detected. Shown in Figures 6 and 7 below, the primary polymer signals from the starting mixtures decreased to baseline after 30 days of thin film ambient exposure. The loss of these polymer signals suggests possible surface cross-linking into larger species. Nipol polymers contain random butadiene and acrylonitrile repeat units in which peak sets are separated by 54 and 53 Daltons,

respectively. It may be that the primary peak sets, which diminish after 30 days exposure, have undergone oxidation or contain more cross-linking capability with a greater ratio of butadiene repeat units in the optimal conformation. Notably, the signals shown here demonstrate only a fraction of the total polymer and may not represent NBR in different mass ranges. Other factors for these MALDI MS signal differences must be considered, such as ionization efficiency and substrate reactions

As shown in Figure 6, multiple polymers were detected. The three NBR films were made with different numbers of formulation additives at formulation ratios, but exhibited similar spectra. The primary peak sets, highlighted in orange, are absent in the exposed films. Pure Nipol polymers, NBR and low-viscosity NBR, were also analyzed for verification. The mass difference between the primary peaks in the starting mixture and the exposed film is 16–18 Da—suggesting oxidation of the polymers. The mass spectrum from pure Nipol, particularly low mass polymer, was similar to that of the starting mixtures. Mentioned above, it may be that the primary peaks contained more butadiene repeat units in ideal conformation and are more conducive to oxidation/cross-linking. Separate analyses by Pyrolysis Gas Chromatography (PyGC)/MS and Nuclear

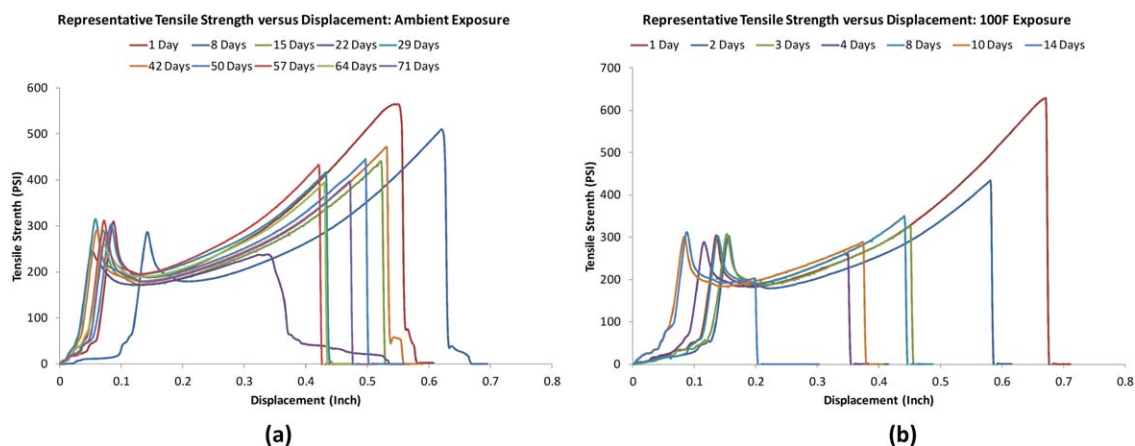


Figure 10. (a) Ambient and (b) 100°F exposure tensile load traces as a function of exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 11. (a) 1-day, (b) 8-day, and (c) 29-day ambient exposure panels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Magnetic Resonance Spectroscopy (NMR) confirmed the butadiene : acrylonitrile ratio at $\sim 2 : 1$. At higher masses, the spectra become less complex and the distinction between Nipol polymer signals from the mix and film become clearer. Mass spectra above m/z 3300 from mix/film #2 are shown in Figure 7. The polymer signal differences between starting mixtures and exposed film are clearly seen.

All films gave similar spectra, despite containing different constituents, suggesting that any reactions may be a consequence of the 30-day ambient exposure. Again, a peak separation of 16–18 Da was observed between major peak sets of the fresh mix and 30-day exposed film. The change in Nipol polymer signals may indicate oxidation and cross-linking, which could affect surface behaviors of PBI-NBR.

Bond Performance

Results of the bond test panels show a correlation between uncured PBI-NBR exposure conditions with peel and tensile adhesion performance. Applying the HPLC/MS findings to this correlation implies a distinct relationship between bond performance and tallow amine content, and possibly tackifier content. Extended exposure of this material to ambient conditions (68°F) increases tallow amine surface concentration and causes a shift from cohesive insulation failure to thin film rubber, which corresponds to a decrease in both peel and tensile strength. This effect appears to be accelerated with elevated temperature conditioning at 100°F, indicating temperature dependence of rubber constituent diffusion.

The median of average peel strength and median of maximum tensile strength as compared to wt % tallow amine is shown in Figure 8. The wt % tallow amine depicted in Figure 8 coincides with time (days) of exposure shown previously in Figure 5. These data are reasonably fitted by linear regressions, as indicated by the higher R^2 values. Representative load traces are shown in Figures 9 and 10 for peel and tensile specimens, respectively. Only one representative load trace is shown since replicates were tested at each condition. Pictures of the 1-, 8-, and 29-day ambient exposure test panels are shown in Figure 11. Inspection of the load traces and failure modes shows a definitive decrease in bond performance over time.

Peel mode appears to be much more sensitive to conditioning than tensile mode, as indicated by comparing the loss of capability in Figure 8. This sensitivity is shown with ambient exposure, but is

more significantly demonstrated with 100°F conditioning. As little as one day of 100°F conditioning resulted in loss of significant peel strength capability. HPLC/MS results indicate that tackifier components diffuse to the surface (in addition to tallow amine) with 100°F conditioning and therefore likely contributed to these observations. However, proportional tackifier component diffusion was not observed with ambient conditioning.

CONCLUSIONS

The releasing properties of tallow amine, along with surface oxidation of the NBR polymer, may be contributing to weakened bonding issues observed with the NBR formulation containing tallow amine.

Exposure of uncured NBR formulation containing tallow amine treated organo-montmorillonite nanoclay results in measured changes and concentrations of surface species and contributes to adhesive bond failures with a metal substrate. Amphiphilic quaternary tallow amine is observed to accumulate at the surface of uncured rubber upon exposure to ambient conditions. Along with tallow amine, the formulation tackifier also accumulates when the temperature is increased slightly to 100°F. Further, the NBR polymers exposed to ambient air exhibit a mass shift suggesting oxidation or cross-linking of surface species. These measured chemical changes are implicated as contributors to adhesive failures between vulcanized NBR and metal bond surfaces.

As a result of these investigative test efforts, measures have been implemented to protect the bond surfaces of PBI-NBR insulation.

Follow-on work to this research could include experimental quantification and diffusion modeling of the tallow amine concentration gradient through the rubber profile, not just surface accumulation. Further studies of the films analyzed by MALDI-TOF/MS under additional environmental stresses, such as elevated temperature and humidity, may help to verify suspected reactions.

ACKNOWLEDGMENTS

This work was supported by NASA contract NNM07AA75C. The authors are grateful for technical discussions and input from Ping Li, Himansu Gajiwala, and Ken Spaulding, and to Kathy Shafer for editing the manuscript.

The three listed authors each contributed to the technical content and editing of the stated work. Shawn Parry performed the

chemical analyses, HPLC/MS, and MALDI/MS. Justin Pancoast and Scott Mildenhall performed mechanical bonding tests. All three authors completed data analysis of their respective tests and contributed in generation of the manuscript.

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