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Rad res manuscript

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Abstract

By incorporating CNTs and graphene nanomaterials with aromatic sp2 carbon structures (Figure 1), we have specifically tuned filled EPDM seal and gasket composite materials for radiation resistance. Our results show that CNTs and graphene have an increased ability to stabilize the EPDM matrix compared to standard CB as a radiation resistant filler. Graphene outperforms both CNT and carbon black (CB) fillers when considering surface damage under conditions where beta exposure is an issue. Both graphene and CNT fillers offer significantly reduced changes in glass transition temperature under prolonged exposure to tritium compared to CB filled standards, with a 2.5-fold and almost 5-fold reduction, respectively. Thus, CNT and graphene filled O-ring materials could be designed that would maintain acceptable seals significantly longer than currently used composites

Introduction

Polymers posess unique properties, including processibility and high compliance/conformality, that are indespensible for sealing applications in gas vessels. The Tritium Facility is in need of a more radiation-resistant elastomer(s) that will prolong the service life of valve seals, O-rings, etc., and subsequently reduce the number of change outs and volume of gas leakage. Ethylene propylene diene monomer elastomer (EPDM), , is utilized extensively in these applications. Carbon fillers have been shown to reduce effects of radiation exposure on the polymer matrix [1]. By adding known β-resistant carbon nanotubes (CNTs) and graphene as “antirad” fillers, damage from beta exposure may be reduced even further. The regular ordered structures seen in CNTs and graphene are known to be more resistance to radiation damage than the traditional carbon black (CB) [2,3]. The improved radiation tolerance arises because of aromatic carbon’s high resistance to radiolysis.This increased resistance is a result of resonant stability of the π-bond network and increased interaction cross-section due to the delocalized nature of the bonding orbital. The literature reports resistance to beta flux in the electron microscope an order of magnitude higher for π-bond structures compared to linear polymers [4]. The addition of aromatic rings through copolymerization or blending of styrene into isobutylene and polyethylene systems, confers increased radiation tolerance up to very high loadings of 80 wt% [5,6]. Moreover, the resistance is seen to exceed volumetric average predictions and functions most strongly for closely located moieties, indicating a protective effect from the aromatic ring, rather than simple reinforcement.

Procedure

Materials

CNTs and graphene (seen before mixing in the left and right of Figure 1, respectively) were produced or procured and mixed into EPDM samples as described below in the sample preperation section. The quality of dispersion of the filler was evaluated via SEM imaging (Figure 4) and mechanical measurements (Figure 2). Poor contrast between carbon based fillers in a carbon based polymer matrix in the SEM leads to some difficulty in direct confirmation of the dispersion state. Because of this, we are unable to quantitatively compare the dispersion of the filler in different systems, and only qualitatively state it is past an acceptable threshold. Reproducable mechanical data also indicates that the sample materials are consistent, supporting that consistent dispersion has been achieved. Tensile data such as that in Figure 2 was used to iteratively select loadings of CNT and graphene, which would lead to mechanical properties comparable to CB at the standard loading of 32 wt%.

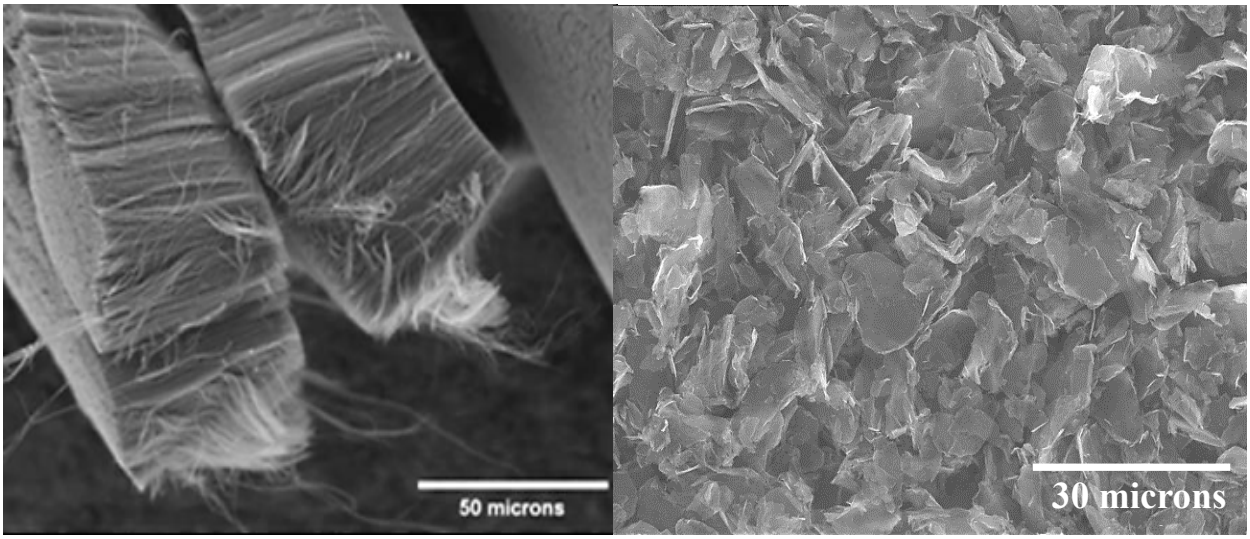

Figure 1: SEM micrographs of vertically aligned CNT (left) produced at Nanotech Labs and multi-layer-graphene platelets (right) purchased from Angstron Materials

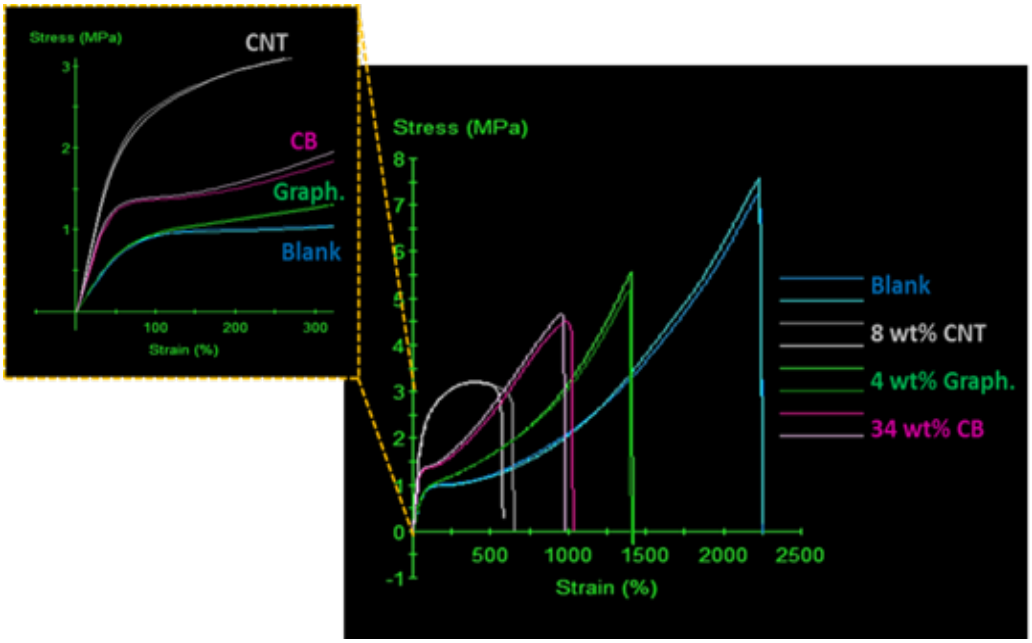

Figure 2: Example tensile test data for initial loading selections of CNT, graphene, and CB loaded EPDM

Sample prep

A typical procedure for creating samples was as follows (See Figure 3): a known quantity of EPDM rubber was dissolved into an organic solvent, typically hexanes, at a 1:5 ratio of solids to solvent by weight. Manufacture recommended curing agents were then added at the recommended ratios, along with any desired fillers (i.e., graphene, CNTs, CB). The blend was mixed in a FlackTec speedmixer. Once the components were well mixed, the hexane was removed in a vacuum oven overnight. The resulting formulation of uncured composite rubber was added to a mold for hot pressing and vulcanization. It was found that high quality samples were best achieved with a two-step process. Initially, the press is heated to 120°C and light pressure applied for approximately 15 minutes to allow the rubber to soften and flow into the mold. After excess rubber and gas escapes the mold, applied force could be increased to 10,000 lbs. and temperature increased to 165°C for 15 minutes to promote vulcanization. Pressure was

maintained while the samples slowly cooled to ambient temperature. After cooling, the sample was removed from and mold and cut into desired shapes.

Figure 3: A variety of filled EPDM composites were formulated along with blank EPDM rubber containing no filler as listed in Table 1. They were chosen to investigate the effect of both type of filler and filler concentration.

Table 1. Example filler loadings under investigation

Filler	Concentration (wt %)
Carbon Black	32
Graphene	2-8
Carbon Nanotubes	2-8

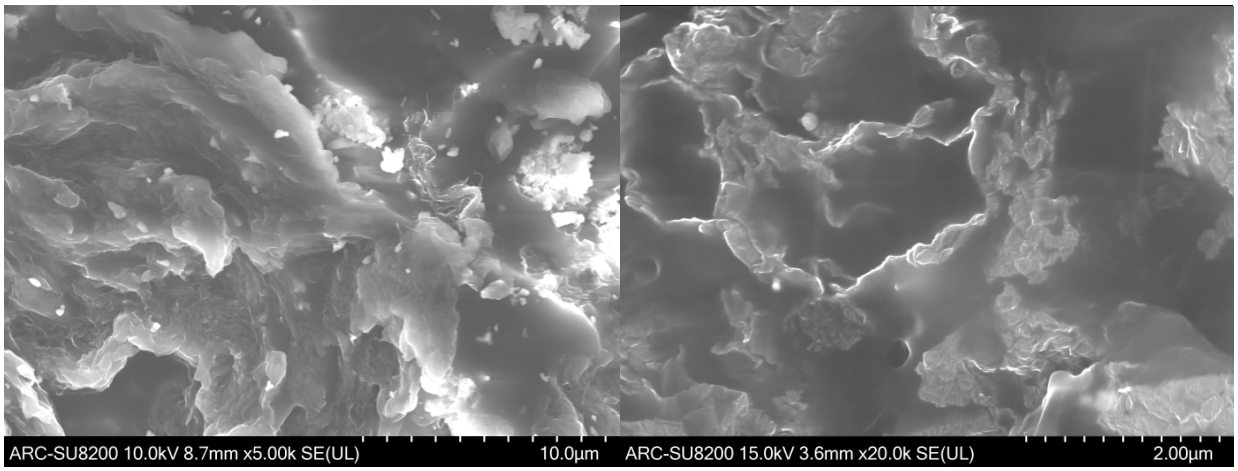

Figure 4: SEM micrographs of a low magnification (left) and high magnification (right) from a mixed composite with graphene and CNT as filler. Bright lines that appear as threads are CNT, and the bright non-topographical edges are attributed to graphene flake edges.

Tritium and β-surrogate exposure

Three different techniques were selected for simulating exposure to tritium. High pressure and temperature H_2 gas was selected to simulate chemical effects, while electron beam exposure and 90Sr/90Y were selected as alternative sources of beta radiation. Dogbone samples were punched from coupons of each composite formulation of interest for these exposures to accommodate mechanical testing. Protium (H_2) exposures lasted for 72 hours at 90°C and 1000 psi. 90Sr/90Y exposures lasted for 3 and 6 weeks. Because the energies associated with beta decay in 90Sr/90Y (546 keV) are much higher than those from tritium (average 5.7 keV with a tail approaching 20 keV), e-beam exposures in SEM at 20keV and 30 µA at 100x magnification for a 2 hour duration were also conducted. Select samples were also exposed to tritium at ambient temperature and pressure.

Materials Characterization

Swell Tests

DMA – A TA Instruments DMA 2980 Dynamic Mechanical Analyzer was used to assess storage and loss moduli in the glassy and rubbery states for low strains. After the temperature stabilized at the selected low temperature, the sample was allowed to equilibrate for 10 minutes to insure a consistent temperature profile. Temperature was then ramped at 2°C/min from -70°C to room temperature while the sample was swept with a mechanical stimulus at a frequency of 1 Hz.

1. Amplitude?

Tensile tests - Tensile tests were conducted on dogbone samples punched from sample coupons with nominal 10 mm gauge length, 2.5 mm width, and a thickness of 1-2mm that was dependent upon the parent coupon. The tests were conducted in a MTS tensile tester.

TGA – A Shimadzu DTG-60 simultaneous DTG-TG instrument was used to gather TGA measurements under a nitrogen atmosphere. After equilibrating at 90°C and holding for 10 minutes, the samples were ramped at 10°C/min to a final temperature of 800°C while the mass of the sample were recorded.

AFM - Atomic force microscopy was used to evaluate swelling and erosion of composite sample surfaces after e-beam exposure in the SEM. More Detail???

Results and Discussion

Baseline Material

Swell tests and quality control

After selecting appropriate loadings of CNTs and graphene, swell tests and tensile tests revealed that the fabricated samples, regardless of filler, exhibited similar swell ratios and moduli (see **Table 2**). This confirms that the selected loadings yield similar crosslinking densities and mechanical properties, indicating that comparisons from later tests will be relevant. The fact that the fillers did not significantly alter the crosslinking of the matrix indicates that substantial property changes are due solely to the presence of the filler and its properties, rather than a conflated second order alteration of matrix behavior. Additionally, similar loadings have been shown to produce comparable Tg values to the matrix, listed in **Table 3**.

Table 1: Swell Ratio and Modulus from example composites

Sample	Swell Ratio	Modulus (MPa)
CB 32%	0.54	11
CNT 6%	0.59	11
Graphene 4%	0.61	14
CNT and Graphene 2%+3%	0.67	12

Table 2: T_g from example composites

Sample	Glass transition temperature (Tg)/ °C
Unfilled	-50.8
Carbon Black filled	-51.4
Carbon Nanotube filled at 8%	-49.7
Carbon Nanotube filled at 4%	-51.0
Graphene filled at 8%	-50.9
Graphene filled at 4%	-44.4

TGA

TGA results (see **Figure 5**) on the baseline EPDM and composites reveal significantly different thermal decomposition behavior. CB and graphene loaded EPDM samples display minor off-gassing at

temperatures between 100-200°C (**Figure 5** insert), while CNT loaded EPDM does not exhibit any additional off-gassing over that of the unloaded EPDM. This may be due to residual solvent not fully removed from the graphene loaded sample. Additionally, all the filled composites delay the primary decomposition peak of EPDM. For CB loaded samples, the EPDM matrix decomposition is delayed from ~450°C to ~475°C and an additional decomposition appears at higher temperature due to the significant loading of CB itself. EPDM breakdown is also delayed by ~25°C in the case of graphene and CNT filled EPDM. Delayed thermal degradation is attributed to bound layers of EPDM near the filler surface obtaining enhanced stability by that association.

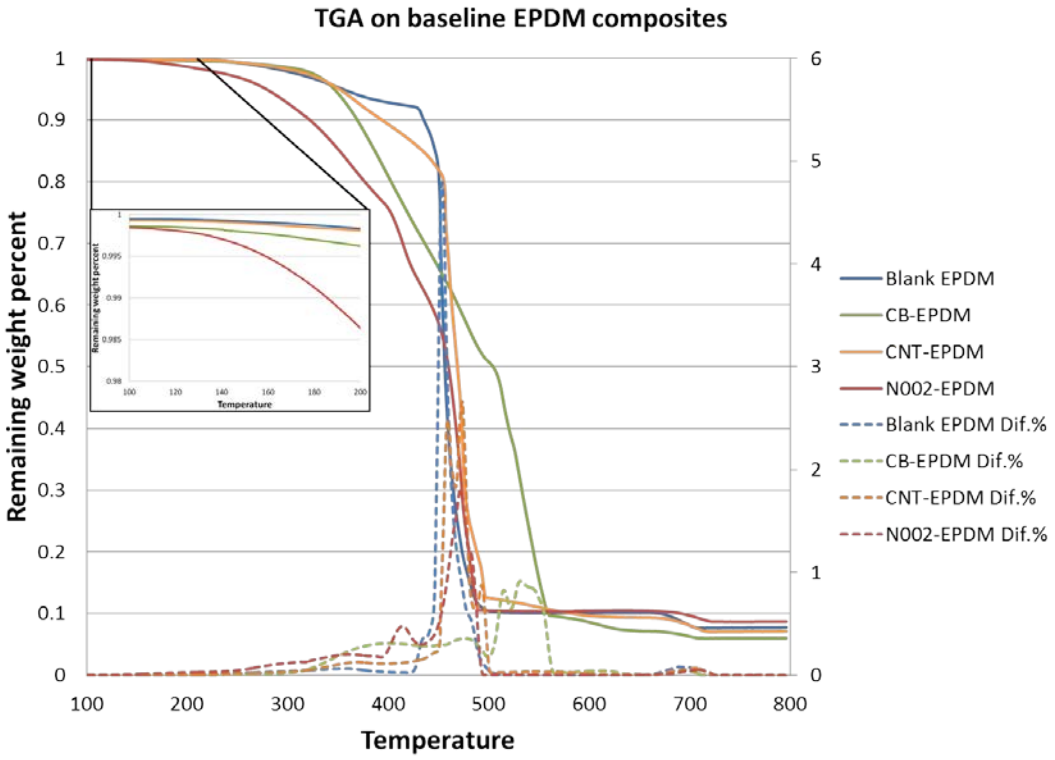

Figure 5 TGA data giving remaining weight percent (solid lines) and rate of weight loss (dashed lines) from 100 to 800 Celsius.

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Results from $^{90}Sr/^{90}Y$ Exposed Material

The mechanical properties of samples exposed to high energy β irradiation from a $^{90}Sr/^{90}Y$ source at Clemson University were investigated. DMA was again used to measure storage and loss modulus. Significant changes were not seen in the rubbery or glassy plateaus of any system. Additionally, the peak in loss tangent was not seen to change in the blank, CB loaded, or the CNT loaded composites. However, the tanδ peaks of the graphene loaded composite (see inFigure 6) increased from -32°C to -29°C after 3

weeks and to -24°C after 6 weeks. This indicates an increase in relaxation time related to main chain motion, which likely arises from crosslinking due to radiaiton exposure.

InFigure 7, tensile tests on the blank EPDM and CB and CNT loaded composites indicate that there are further mechanical effects in these systems despite the lack of change in T_g. In both the blank and CB loaded composite, a stiffening at high strain and reduction in the extension to failure is observed. Conversely, while CNT loaded composites also show a slight stiffening, the strain to failure increases, revealing an increase in toughness not seen in the control materials.

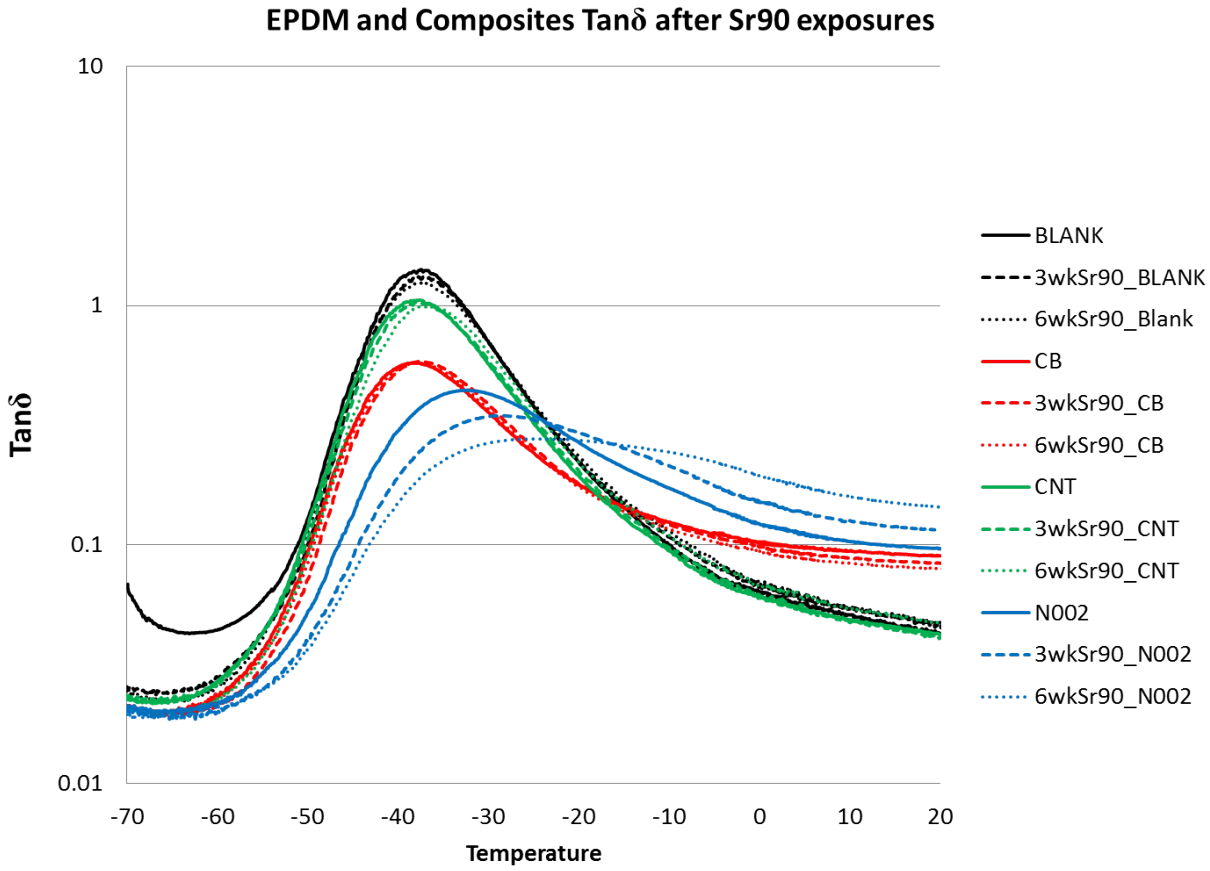

Figure 6: Tanδ data from DMA measurements of EPDM and composites after 3 and 6 week exposures to a $^{90}Sr/^{90}Y$ 20 mCi source at Clemson

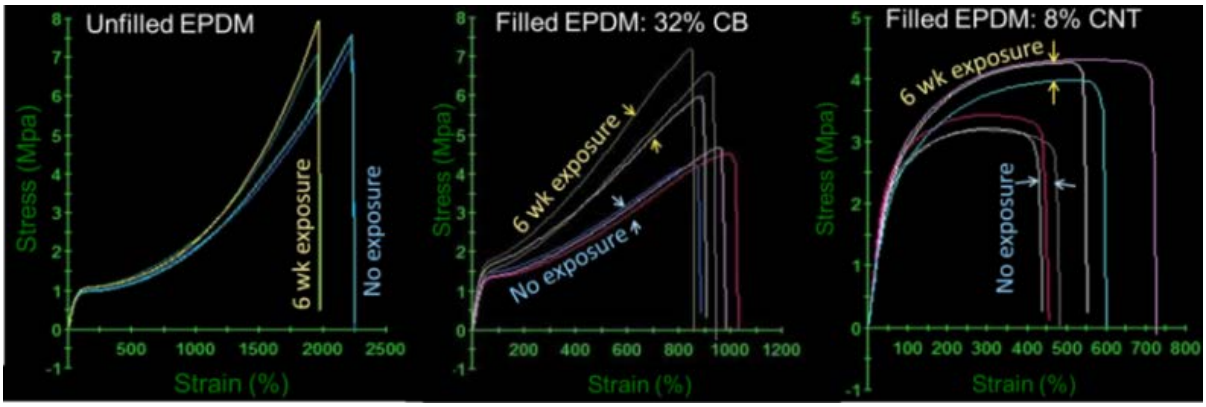

Figure 7: Stress strain data on EPDM composites measured before and after a six-week β exposure under a $^{90}Sr/^{90}Y$ 20 mCi source at Clemson, examples of filled and unfilled EPDM composites produced at SRNL.

Results from SEM simulated β exposure

Because the energies associated with β radiation from a $^{90}Sr/^{90}Y$ source are two orders of magnitude higher than those seen in tritium, an alternate method was chosen to more closely replicate those radiological conditions to examine the effect of a more energetically comparable radiaiton source from the SEM. The SEM provides a better analogue to the β exposure from tritium because of the tunability of the e-beam in the SEM.. However, it interacts with the sample surface and does not penetrate the sample in the same fashion tritium gas would, and thus cannot provide useful bulk data. Thus, AFM was used to investigate the effect on the sample surface after e-beam exposure. This allows for an indication of how the bulk material will be affected as it is exposed to permating tritium gas and subsequent β decay.

Figure 8displays optical micrographs of the setup, where a copper TEM grid was used to shield a grid of the sample from the electron beam, as well as exposure results on unfilled EPDM and graphene filled EPDM. The unfilled EPDM reveals that the pattern from the copper TEM grid used as a shield has been transferred to the polymer, but the graphene loaded material displays no such patterning under the same exposure conditions.

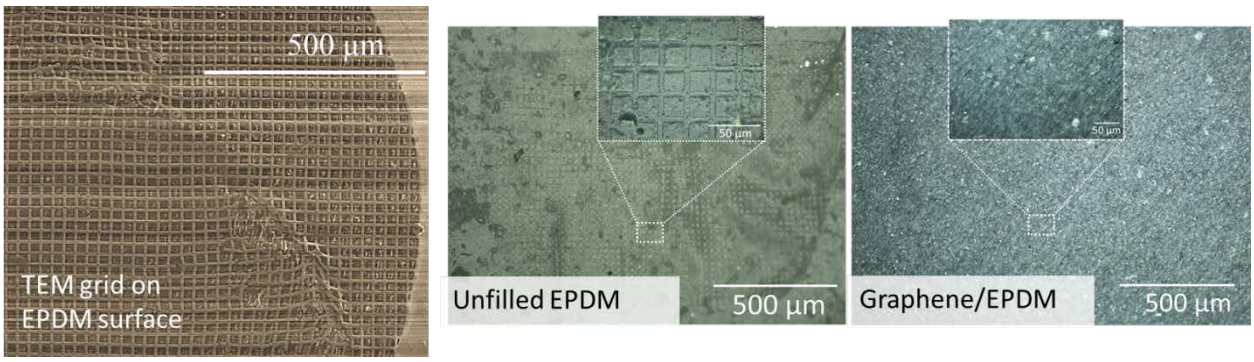

Figure 8: SEM image of EPDM (left) with TEM grid shielding/exposing its surface to e-beam. This technique enables control of the b energy (1-20keV) and flux (b /cm2). Optical microscopy images show significant surface etching of the unfilled EPDM (center) and no degradation for the graphene filled EPDM (right).

AFM allows closer examination of this phenomenon (see Figure 9, Figure 10, Figure 11, and Figure 12).These figures display the swelling and formation of the negative of the TEM grid pattern that occurs in both 32% CB loaded EPDM and in poorly dispersed 8 wt% CNT loaded EPDM. Improving the dispersion of the CNTs improves the resistance to e-beam damage (compare Figure 10 to Figure 11). Graphene loaded EPDM is seen to completely resist the damage from the e-beam exposure, even at half the loading necessairy in the CNT composite.

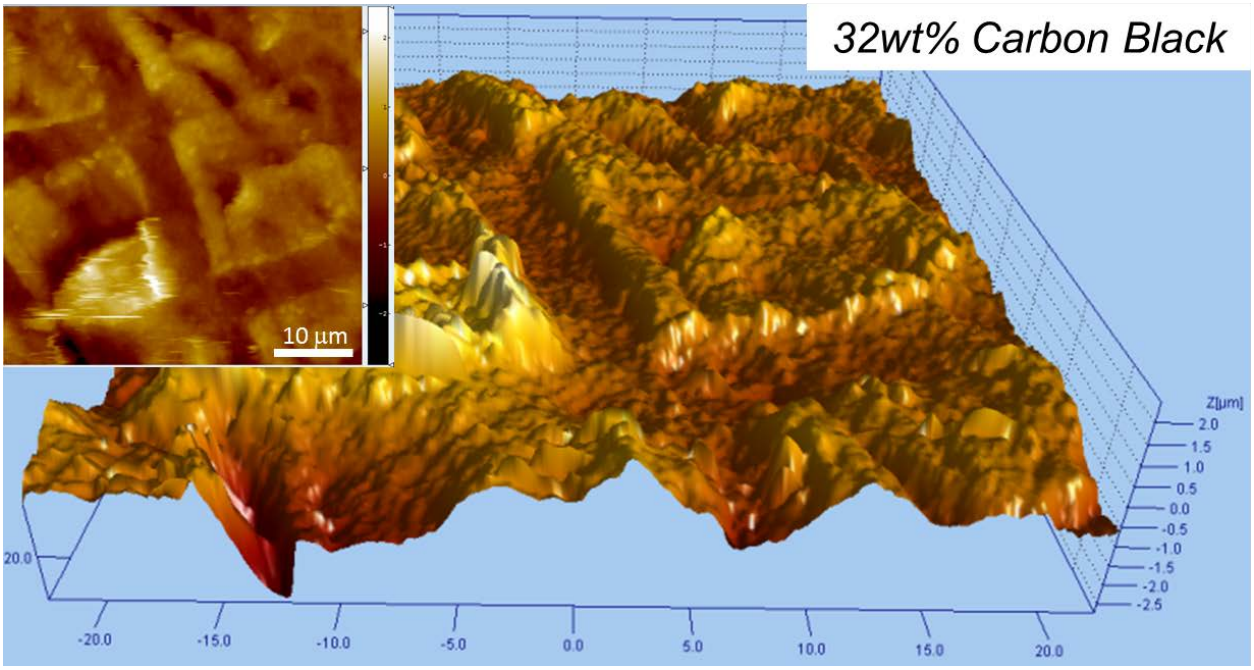

Figure 9: AFM data from 32 wt% CB loaded EPDM after e-beam exposure in the SEM

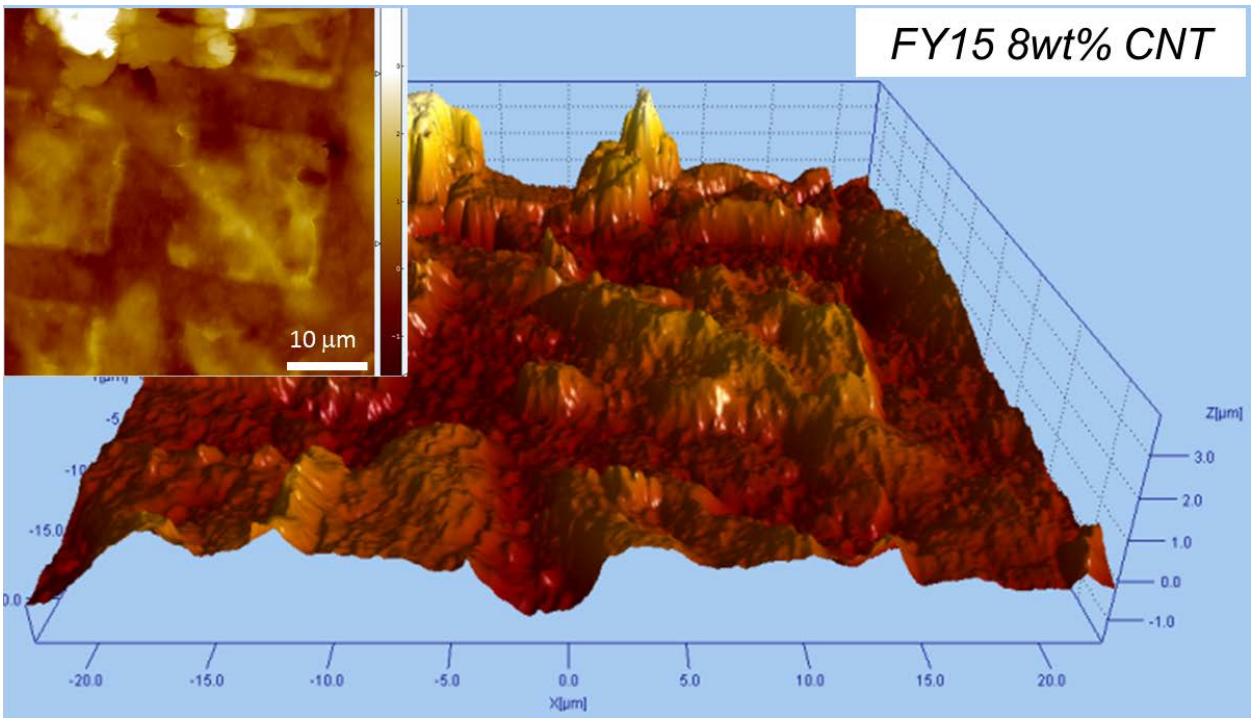

Figure 10: AFM data from 8 wt% CNT loaded EPDM created in FY15 after e-beam exposure in the SEM

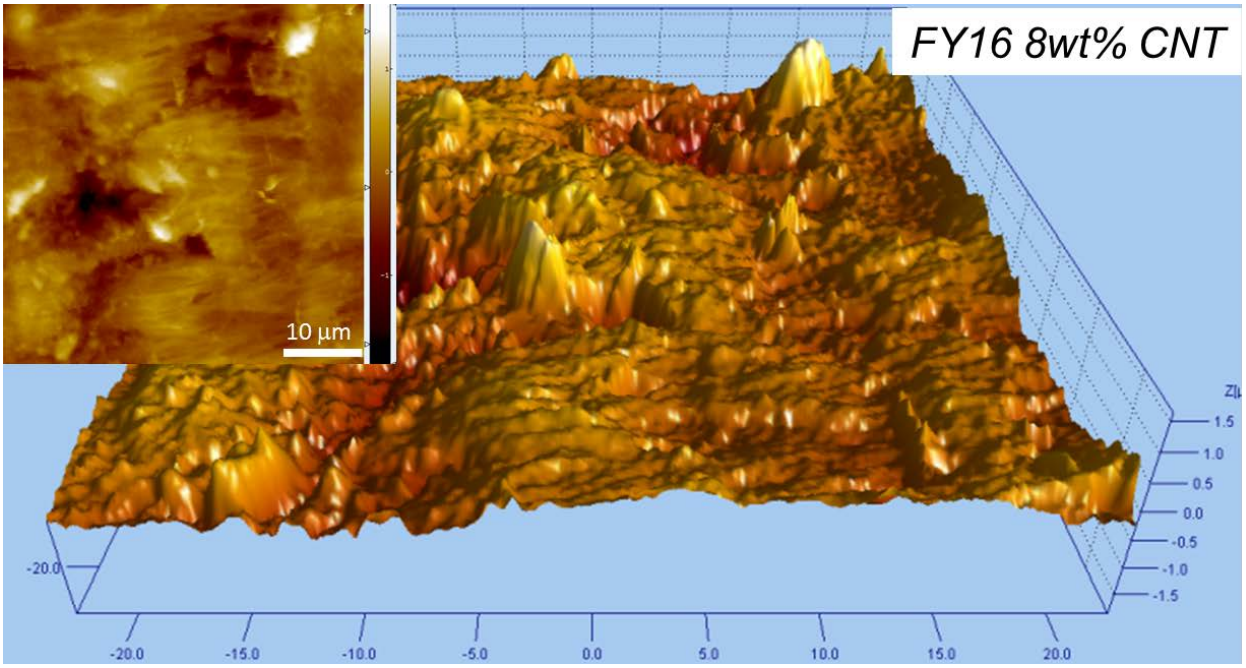

Figure 11: AFM data from 8 wt% CNT loaded EPDM created in FY16 after e-beam exposure in the SEM

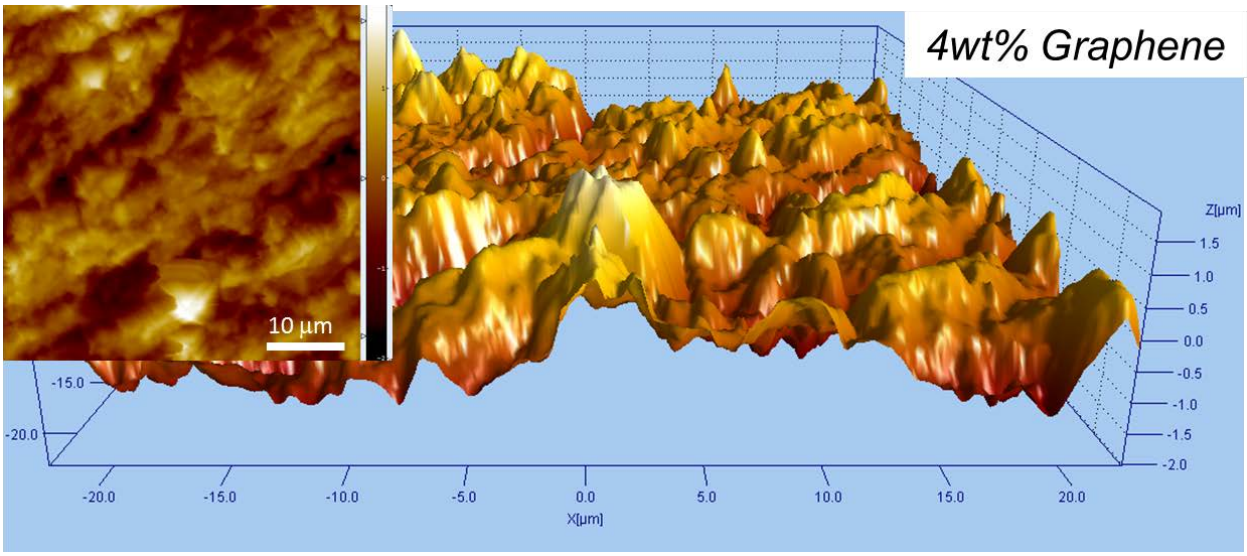

Figure 12: AFM data from 4 wt% Graphene loaded after e-beam exposure in the SEM

Tritium exposures

Select samples were exposed to tritium for periods of time longer than 300 days. While they ended up too brittle to be meaningfully tested in a traditional tensile test, data could be extracted from the less fragile samples via DMA measurements. The glass transition temperatures and percent change thereof are compared in Table 4and reveal substantially reduced changes with the introduction of nano-carbon fillers.

Table 3: Glass transition temperatures pre- and post-T_2 exposure for select EPDM samples

Sample	T_g (°C) pre-exposure	T_g(°C) post-exposure	% change
Unfilled	-50.8	-24.0	52%
Carbon Black filled	-51.4	2.6	105%
Carbon Nanotube filled at 8%	-49.7	-38.7	22%
Graphene filled at 8%	-50.9	-30.1	41%

Conclusion

From these data, it can be concluded that CNT loaded EPDM provides the best resistance to thermal degradation compared to graphene and carbon black fillers, as well as the neat polymer. Additionally, CNTs provide increased resistance to very high energy β radiation compared to carbon black loaded EPDM. This is thought to be a results of the aromatic carbons higher resistnace to radiolysis and its increased stability due to π-bonding. Graphene provides the best resistance to surface damage from β radiaiton at energies

relevant to tritium exposure, while CNT fillers better resist changes to the glass transition temperature in actual tritium conditions, showing almost a 5 times smaller change than the industry standard, carbon black filler. Both CNT and graphene fillers display these benefits at loadings of only a fraction of those necessairy for traditional carbon black. Finally, it should be noted that no single simulating test captures the low energy, full sample β exposure that tritium produces and no effective way to simulate helium evolution was found.