

**FIRST STEP TOWARD A RADICAL POLYMER-BASED CONDUCTIVE
ENERGETIC MATERIAL**

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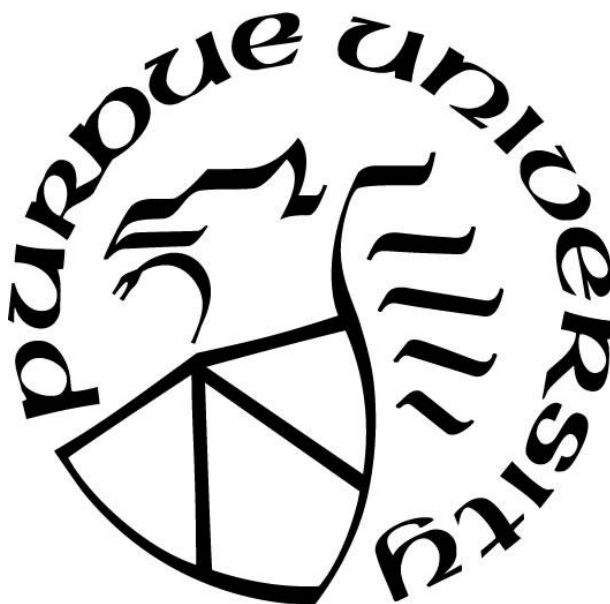
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To my wife, Meg

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TABLE OF CONTENTS

LIST OF FIGURES	7
ABSTRACT.....	9
1. INTRODUCTION TO ENERGETIC COMPOSITES AND ELECTRICALLY CONDUCTIVE POLYMERS	10
1.1 General Introduction.....	10
1.2 Plastic Bonded Explosives	10
1.2.1 Processing.....	10
1.2.2 Effect of Binder on Mechanical Properties and Sensitivity	11
1.2.3 Effect of Strain Rate and Temperature on Mechanical Properties and Sensitivity .	13
1.2.4 Effect of Particle Size Distribution on Mechanical Properties and Sensitivity.....	14
1.3 Composite Propellants.....	16
1.3.1 Mechanical Properties	16
1.3.2 Effect of Temperature on Ignition Behavior	17
1.4 Summary of Energetic Composites	17
1.5 Electrically Conductive Polymers	18
1.5.1 Conjugated Polymers	18
1.5.2 Radical Polymers.....	21
1.6 Summary.....	22
1.7 References	23
2. FIRST STEP TOWARD A RADICAL POLYMER-BASED CONDUCTIVE ENERGETIC MATERIAL	31
2.1 Introduction	31
2.2 Experimental.....	33
2.2.1 Materials.....	33
2.2.2 General Methods	33
2.2.3 Synthesis.....	34
2.2.4 Mock PBX Formulation	35
2.2.5 Dynamic Mechanical Analysis.....	36

2.2.6	Electrical Conductivity Testing.....	36
2.3	Results and Discussion	37
2.4	Conclusions	49
2.5	Supplementary Information.....	50
2.6	References	61
3.	CONCLUSIONS AND FUTURE WORK.....	66
3.1	Conclusions	66
3.2	Future Work.....	66
3.3	References	68

LIST OF FIGURES

Figure 2.1. (a) PTEO-GBP before (left) and after (right) UV crosslinking. PTEO-GBP can either form an alkylbenzhydrol (top) or benzopinacol species (bottom). Wavy lines represent the rest of the polymer not shown in the crosslinked structures. (b) FTIR spectra of PTEO-GBP before and after UV exposure. An increase in the intensity of the alcohol stretch at $\sim 3500\text{ cm}^{-1}$ indicates that UV crosslinking forms alcohol groups.	37
Figure 2.2. DSC thermograms of PTEO and PTEO-GBP (a) before and (b) after thermal treatment. Before thermal treatment, PTEO-GBP has a reduced T_g compared to PTEO. After thermal treatment, its T_g increases to a similar or higher temperature compared to PTEO. PTEO-GBP(X) signifies a polymer with X% GBP, on a molar basis. Endotherms are displayed in the upward direction.	39
Figure 2.3. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ versus temperature for thermally treated neat polymer samples. PTEO-GBP(X) indicates a copolymer with X% GBP, on a molar basis.....	40
Figure 2.4. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ vs temperature for UV-treated neat polymer samples. PTEO-GBP(X) indicates a copolymer with X% GBP, on a molar basis.	42
Figure 2.5. DMA results of 90% sugar-10% polymer composites (by weight) without UV treatment. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature. The legend indicates the percentage of GBP in the polymer, on a molar basis, used as the binder.....	44
Figure 2.6. DMA results of 90% sugar-10% polymer composites before and after UV treatment. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature. Legend indicates the percentage of GBP, on a molar basis, in the polymer used as binder. Samples denoted as “-UV” received the UV treatment.	46
Figure 2.7. DMA and electrical conductivity results of sugar/PTEO/AgNW composites. All of the composites contained 90% solids content. For example, AgNW(3) is composed of 3% AgNWs, 87% sugar, 10% PTEO, on a mass basis. All of the PTEO used was PTEO homopolymer. Sample denoted as PTEO in the legend did not contain AgNWs. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ of composites versus temperature. (d) Conductivity of the composites as a function of nanowire loading.	48
Figure 2.S1. Chemical structures of polymers used as binders. Left: PTEO. Right: PTEO-GBP.	50
Figure 2.S2. NMR Characterization of GBP. (a) Full spectrum. (b) Aromatic region of the spectrum.	51
Figure 2.S3. NMR Characterization of PTEO.	52
Figure 2.S4. NMR Characterization of PTEO-GBP.	52
Figure 2.S5. FTIR characterization of TEO, GBP, and PTEO-GBP.	53
Figure 2.S6. EPR Characterization of PTEO and PTEO-GBP.	53

Figure 2.S7. SEC traces of PTEO and PTEO-GBP polymers. The synthetic procedure produced consistent molecular weights. PTEO-GBP(12.6) had an anomalous molecular weight distribution, resulting in a significantly higher glass transition temperature as determined by DMA. Number average molecular weight (M_n) of PTEO = 4720 g/mol, Polydispersity (PDI) of PTEO = 2.25. PTEO-GBP(2.6) M_n = 5150 g/mol, PDI = 1.88. PTEO-GBP(8.5) M_n = 5073, PDI = 1.77. PTEO-GBP(12.6) first peak M_n = 152354 g/mol, PDI = 2.72. PTEO-GBP(12.6) second peak M_n = 2316 g/mol, PDI = 3.30.	54
Figure 2.S8. DSC thermograph of PTEO-GBP(19.4) exhibiting two apparent glass transitions at $\sim 0^\circ\text{C}$ and $\sim 40^\circ\text{C}$	54
Figure 2.S9. Frequency sweep DMA experiments of neat PTEO-GBP(3.8) and PTEO-GBP(16.3) samples after UV crosslinking. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ is plotted from 10^{-2} to 10^2 Hz.	55
Figure 2.S10. DMA of a composite composed of 90 wt% sugar and 10 wt% PTEO-GBP(8.5) as the binder. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ plotted versus temperature.	56
Figure 2.S11. Conductivity of composites composed of 87 wt% sugar, 10 wt% binder, and 3 wt% AgNWs. Conductivities of the composites are displayed when PTEO, PTEO-GBP(1.8), and PTEO-GBP(5.1) was used as the binder.	57
Figure 2.S12. DMA of composites composed of 87 wt% sugar, 10 wt% PTEO-GBP binders, and 3 wt% AgNWs. The binders used were PTEO-GBP(1.8) and PTEO-GBP(5.1). (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature.	58
Figure 2.S13. Pictures of DMA samples. <i>Left Image</i> : Neat PTEO-GBP sample (left) and neat PTEO homopolymer sample (right). <i>Middle Image</i> : 90% Sugar/10% PTEO sample (left) and neat PTEO-GBP sample (right). <i>Right Image</i> : 87% sugar/10% PTEO/3% AgNW sample. All of the samples are $\sim 30\text{mm} \times 7\text{mm} \times 1\text{mm}$ besides the PTEO homopolymer sample.	59
Figure 2.S14. Optical microscopy images of 87% sugar/10% PTEO/3% AgNW sample. (a) Sugar crystals visible in PTEO matrix. (b),(c) AgNWs visible on the surface of sugar crystals.	60

ABSTRACT

Plastic bonded explosives (PBXs) and composite propellants (CPs) have yet to fully leverage the electrically conductive capability of polymers and nanomaterials. A PBX or CP with a high degree of electrical conductivity could be utilized for many different applications. In this work, an electrically conductive radical polymer is used as a binder in mock PBX formulations. Specifically, poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) was copolymerized with glycidyloxy-benzophenone (GBP) to create PTEO-co-GBP (PTEO-GBP), and this was blended with sugar, which acted as a solid energetic simulant. Crosslinking of PTEO-GBP and the sugar-PTEO-GBP composites revealed both thermal and UV curing mechanisms for the polymer. Finally, silver nanowires (AgNWs) were added to impart macroscale conductivity to the mock PBX composites. Due to the intrinsic conductivity of the PTEO moiety, only low loadings of AgNWs were required to observe an electrical conductivity of $\sim 1 \text{ S cm}^{-1}$. Additionally, this level of AgNWs mechanically reinforced the composite, producing a mechanically robust mock PBX. Thus, this study presents the first step in developing a highly conductive energetic composite that utilizes a radical polymer as the binder and is capable of being resistively heated.

1. INTRODUCTION TO ENERGETIC COMPOSITES AND ELECTRICALLY CONDUCTIVE POLYMERS

1.1 General Introduction

Composite energetics are a broad class of materials that are composed of high energy solids distributed in a polymer binder. Plastic bonded explosives (PBXs) are a subcategory of composite energetics where the energetic particles are high explosives that are capable of violent detonation.^{1,2} On the other hand, composite propellants (CPs) are another category of composite energetics where the energetic particles burn (instead of detonating) to produce a sustained flow of hot gases.^{1,3}

This introduction will outline different factors that affect the mechanical properties and combustion behavior in PBXs and CPs. Then, the development of electrically conductive polymers will be discussed. Specifically, conjugated polymers and open-shell radical polymers will be considered with an emphasis on their mechanical properties and how they could impact the field of composite energetics.

1.2 Plastic Bonded Explosives

PBXs contain a high weight percentage of explosive crystals (~85-98%) and a small percentage of polymer serving as a binder.^{1,2,4} Even though these binders are present in small proportions, they have a large impact on the properties of the composite material. Specifically, they provide dimensional stability,^{2,4,5} mechanical strength,^{2,4} and reduced sensitivity^{4,6-9} to the final explosive material. While the binder has a large influence on the mechanical properties and sensitivity of a PBX, other factors affect these characteristics as well. Temperature, strain rate, and particle size all have a strong influence on the mechanical properties of PBXs. Furthermore, temperature and particle size have a pronounced influence on the sensitivity of PBXs.

1.2.1 Processing

PBXs can be processed by a variety of techniques. Two commonly used procedures are the cast-cure and solvent-antisolvent methods. The cast-cure method involves mixing the ingredients – binder, explosive, curing agent, and other ingredients – together, pouring the mixture into a mold,

and giving the mixture time to cure (harden).^{5,6,10} This process is prevented from producing the highest solids loading PBXs due to an increase in viscosity as solids loading increases. Therefore, at very high (>90% by weight) solids loading, the uncured mixture is too viscous to pour into a mold.⁵

Alternatively, the solvent-antisolvent method of mixing explosive crystals and binders can achieve very high solids loading. In this method, the explosive particles are suspended in a non-solvent and the binder, dissolved in an immiscible good solvent, is added to the suspension. The good solvent is evaporated from the mixture and the binder subsequently precipitates onto the explosive particles suspended in the water to form a molding powder.^{11,12} The molding powder is heated (25-150 °C) and pressed (100-200 MPa) to form high-density charges. These charges are then remotely machined to form into the desired shape.¹²

1.2.2 Effect of Binder on Mechanical Properties and Sensitivity

There has been a significant effort devoted to understanding the effect PBX binders have on the mechanical properties of the entire composite. In general, compliant binders produce PBXs with reduced stiffnesses and strengths as compared to PBXs bound with stiff binders.^{4,13-15} PBX 9501 is a PBX consisting of 95% (by weight) octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 5% plasticized Estane binder and PBX-9502 consists of 95% 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 5% Kel F-800 binder. When subjected to tensile loading under identical testing conditions, PBX-9502 displayed a strength of 3.23 MPa compared to 0.78 MPa for PBX 9501.⁴ Considering these two PBXs have the same solids loading, this large difference in tensile strength is explained by the different binders. The plasticized Estane in PBX 9501 has a glass transition temperature (T_g) of approximately -50 °C and the Kel F-800 used in PBX 9502 has a T_g of ~ 30 °C.¹⁶ Therefore, the much higher strength in PBX 9502 is accounted for by its much stiffer, glassy binder compared to the soft, rubbery binder in PBX 9501. In a different study that investigated the mechanical behavior of PBX 9501 and 9502, the compressive modulus and strength as well as the tensile modulus and strength of PBX 9502 was greater than PBX 9501. Additionally, PBX 9501 showed dramatically more creep compliance than PBX 9502.¹³ Thus, binders with higher stiffnesses produce stronger and more dimensionally stable PBXs. Moreover, the proportion of binder in a PBX also influences its mechanical properties. When the percentage of plasticized Estane in PBX 9501 was increased from 5% to 8%, the compressive strength and

modulus decreased at low strain rates ($0.001\text{--}0.45\text{ s}^{-1}$). At high strain rates ($\sim 2000\text{--}2500\text{ s}^{-1}$), however, the increased proportion of binder had little effect on the mechanical strength of the PBX. Though the strength of the PBX at high strain rates was similar with 5 and 8% plasticized Estane, the mechanical response was distinctly different between the two formulations. At high strain rates, the PBX with 8% binder exhibited a much more gradual decrease in stress after the max stress was reached.¹⁴ These high and low strain rate results demonstrate that when a higher percentage of soft binder is used, the PBX displays more ductile behavior.¹⁴ Together, the results from many studies establish the large effect the binder has on the ultimate mechanical properties of a PBX.

In addition to improving the mechanical properties of a high explosive, the binder in a PBX also reduces the sensitivity to undesired insults.^{6,7,9,17,18} Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), a powerful secondary explosive, exhibited significantly reduced impact and friction sensitivities after being coated with a soft, rubbery binder, hydroxyl terminated polybutadiene (HTPB). As determined by a drop hammer test, the impact sensitivity of RDX increased from 37.2 cm to 66.5 cm after being coated with 2% HTPB. Additionally, friction sensitivity tests revealed that the explosion probability of RDX decreased from 92 to 16% after being coated with 2% HTPB. Therefore, HTPB-bound RDX has reduced impact and friction sensitivity compared to RDX.⁷ Also, the sensitivity of a PBX increases as the stiffness of the binder increases. In a series of experiments where HTPB and polydimethylsiloxane (PDMS) were used as binders for PBXs containing 85% HMX and 15% binder, the tensile modulus of the binders was varied by adjusting the binder and amount of curing agent. Above a certain binder tensile modulus ($\sim 2\text{ MPa}$), the drop energy required to ignite the PBXs only decreased slightly. However, when the tensile modulus was reduced below 2 MPa, the drop energy required to ignite the PBX increased precipitously.¹⁷ These results suggest that the impact sensitivity of a PBX decreases as the stiffness of its binder decreases. Furthermore, there could be a threshold stiffness above which the impact sensitivity is relatively unchanged and below which the impact sensitivity decreases steeply.¹⁷ Additionally, impact sensitivity tests conducted on PBXs containing 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), an extremely insensitive high explosive,¹⁹ further revealed the importance of the binder on the sensitivity of PBXs. When a PBX composed of 95% TATB and 5% HTPB underwent an impact sensitivity test, it showed no evidence of ignition. Meanwhile, when a PBX composed of 95% TATB and 5% Kel F-800 underwent the same impact test, it showed evidence of a low order ignition.²⁰ As mentioned above, Kel F-800 is a glassy polymer with a dramatically higher elastic

modulus than HTPB. Therefore, these tests display how a soft binder with a low modulus (HTPB) can dampen energy delivered to an explosive and prevent ignition while a stiff binder (Kel F-800) did not prevent TATB from igniting.²⁰ Together, these studies reveal that binders reduce the sensitivity of PBXs, with compliant binders exerting a greater desensitizing effect than stiff binders.

PBXs are advantageous in certain applications due to the mechanical integrity^{4,13} and decreased sensitivity^{4,6-9} the binder confers to the composite. However, a compromise must be found between the desensitizing and strengthening effect of the binder. Highly compliant binders have a greater desensitizing effect on PBXs than stiff binders.^{6,9,17} Thus, the stiffness of a binder used in a PBX is limited by the sensitivity of the explosive and how much desensitization is needed to make the explosive safe to handle. For example, the secondary explosives HMX and RDX are much more sensitive to shock impulse than TATB.¹⁹ Therefore, HMX and RDX are primarily bound with soft binders that can dampen shock insults and reduce energy delivered to the explosives, making them less sensitive.^{9,18} Alternatively, because of TATB's insensitivity to shock and impact,¹⁹ it can be bound with stiff binders, like Kel-F 800, and remain less sensitive to shock insults than HMX or RDX bound with softer, energy absorbing binders.^{20,21} Thus, the binder used in a PBX must optimize both the mechanical properties and sensitivity of the composite.

1.2.3 Effect of Strain Rate and Temperature on Mechanical Properties and Sensitivity

The strength and Young's modulus of polymers is known to increase with increasing strain rate and decreasing temperature.²²⁻²⁴ This effect is thought to be due to a decrease in polymer mobility at high strain rates and low temperatures that results in a stiffening effect.^{22,25} In general, PBXs also exhibit an increase in strength and Young's modulus as strain rate increases and temperature decreases.^{13,14,26-29} The degree of strain rate and temperature dependence of a PBX's mechanical properties varies depending on the binder. For example, the strength of PBX 9502 increased by a factor of 1.6 when strain increased from 0.001 s^{-1} to 1400 s^{-1} . In contrast, the strength of PBX 9501 increased by a factor of 7 under comparable experimental conditions.²⁹ Furthermore, the strain rate and temperature dependence of Kel F-800 (the binder in PBX 9502) is much less than Estane (the binder in PBX 9501), suggesting the difference in strain rate and temperature dependence of the two PBXs is driven by the strain rate and temperature dependence of the binders.²⁹

In addition to affecting the mechanical properties of PBXs, temperature can also significantly alter the sensitivity of PBXs. The shock sensitivity of LX-04, a PBX composed of 85% HMX and 15% Viton binder, was measured at ambient temperature and 170 °C. The PBX had shorter run distances to detonation at 170 °C compared to ambient temperature, indicating increased shock sensitivity at elevated temperatures.³⁰ HMX undergoes a solid phase transition at ~165 °C, which results in a slight volume expansion of the explosive crystal. Further shock sensitivity experiments elucidated that LX-04 had nearly identical shock sensitivities at 150 °C and 170 °C, suggesting that the increase in sensitivity at elevated temperatures is due to the temperature increase and not the associated decrease in density of the HMX crystals.³¹ Furthermore, the shock sensitivity of LX-17 and PBX 9502, two TATB based PBXs, has been measured at extreme temperatures. In these experiments, it was found that the run distance to detonation decreased as temperature increased for these PBXs, again indicating increased shock sensitivity as temperature increased.^{21,32} Specifically, the shock sensitivity of PBX 9502 and LX-17 at 252 °C was similar to the shock sensitivity of the much more sensitive PBX 9501 at ambient temperature.²¹ Additionally, when shock sensitivity experiments were performed on an RDX-based aluminized PBX, increasing the temperature from ambient to 110 °C resulted in a decrease in shock sensitivity. When the temperature was increased above 110 °C, the shock sensitivity of the aluminized PBX increased.³³ Though temperature clearly affects the sensitivity of PBXs, the effect temperature has on sensitivity varies between different systems.

1.2.4 Effect of Particle Size Distribution on Mechanical Properties and Sensitivity

Another factor that influences the mechanical properties of PBXs is the particle size of the energetic materials. Generally, as particle size of the energetic filler decreases, the strength and modulus of the PBX increase.^{15,34,35} This effect was demonstrated when mock PBX 9501 and PBX 9502 was formulated with 5-iodo-2'-deoxyuridine (IDOX) as the solid filler instead of HMX and TATB particles. These mock PBXs were fabricated with varying IDOX particle size distributions. The PBX 9502 mock material exhibited greater compressive strength and moduli compared to the PBX 9501 mock material, regardless of particle size. The greater strength and stiffness of PBX 9502 was due to the stiff binder, Kel F-800, present in PBX 9502 compared to the soft binder, Estane, used in PBX 9501. The PBX 9501 formulation with the greatest compressive strength and modulus contained the smallest particles used in the study (<75 µm) and the PBX 9501 formulation

with the lowest compressive strength and modulus contained the largest particles used ($>150\text{ }\mu\text{m}$). Similarly, the mock PBX 9502 material with the greatest strength contained the smallest IDOX particles and the PBX 9502 formulation with the least strength had the largest IDOX particles.¹⁵ Additionally, high strain rate stress-strain experiments of PBXs containing 88% (by weight) RDX and 12% HTPB with different RDX particle sizes have been performed. When the average RDX particle size was $159\text{ }\mu\text{m}$, the strength of the PBX was greater compared to a PBX with an average RDX particle size of $710\text{ }\mu\text{m}$. Additionally, the smaller particle size PBX exhibited a less distinct yield point compared to the PBX with larger RDX particles.³⁴ Moreover, when the mechanical properties of a PBX containing 97.5% (by weight) HMX were investigated as HMX particle size was varied, the results again suggest that as particle size decreases, the strength and modulus increase. In this effort, the diameter of HMX particles were $0.1\text{-}0.3\text{ }\mu\text{m}$, $1\text{-}2\text{ }\mu\text{m}$, or $10\text{-}20\text{ }\mu\text{m}$. The compressive strength of the PBX increased from 14.55 MPa to 43.76 MPa when the particle size was decreased from $10\text{-}20\text{ }\mu\text{m}$ to $0.1\text{-}0.3\text{ }\mu\text{m}$. The compressive modulus increased from 0.69 GPa to 1.75 GPa with the same change in HMX particle size.³⁵ Thus, it has been clearly demonstrated that the strength and stiffness of PBXs increase as the particle size of the explosive filler decreases.

The particle size of explosive crystals in PBXs also affects the sensitivity of the composite material. The shock sensitivity of PBXC03 has been investigated as a function of HMX particle size. PBXC03 is constituted of 87% (by weight) HMX, 6.76% TATB, and 7% Viton binder. The particle diameter of HMX was either $20\text{-}30\text{ }\mu\text{m}$, $70\text{-}90\text{ }\mu\text{m}$, or $110\text{-}130\text{ }\mu\text{m}$. Shock sensitivity experiments driven by an external explosive detonation revealed that as HMX particle size decreased, the run distance to detonation decreased, indicating smaller particle sizes result in a more shock sensitive PBX.³⁶ Alternatively, in the PBXs containing 97.5% HMX discussed above, drop hammer impact tests revealed that the impact sensitivity of those formulations decreased as particle size decreased.³⁵ Thus, these two studies suggest that decreasing the particle size of explosive crystals in PBXs increases the shock sensitivity and decreases the low-speed impact sensitivity of a PBX. Another reason for these two seemingly contradictory results could be that the shock sensitivity tests were performed on a PBX with particle sizes in the range of $20\text{-}130\text{ }\mu\text{m}$ while the low-speed impact sensitivity tests were performed on a PBX with particle sizes in the range of $0.1\text{-}20\text{ }\mu\text{m}$. In any case, it is evident that particle size influences the sensitivity of PBXs.

1.3 Composite Propellants

Composite propellants (CPs) are another class of energetic composites that are designed to deflagrate (burn) to generate hot gases and produce sustained thrust.^{1,3} CPs are heterogeneous mixtures of crystalline oxidizer, metallic fuel, and polymeric binders. CP binders are used to hold the different components together, provide mechanical integrity, and act as a secondary fuel.^{3,37} First generation CPs were composed of only a binder and an oxidizer, with the binder acting as the sole fuel source for the oxidizer.³⁸ However, since it was discovered that aluminum powder could increase the specific impulse of CPs,³⁸ it is commonly added to CP formulations.^{3,37,38} Common CPs utilize ammonium perchlorate (AP) as the crystalline oxidizer, aluminum (Al) powder as the fuel, and HTPB as the binder.^{3,38} HTPB is the most commonly used binder due to its superior mechanical and aging properties as compared to other CP binders.³⁷⁻⁴² Furthermore, HTPB has a low viscosity, which permits high solids loading and the ability for the composite to be cast-cured.^{6,42} While PBXs are prepared by the solvent-antisolvent and the cast-curing method, CPs are primarily prepared by the casting method.³⁷ The cast-cure process requires low-viscosity binders, so the end-mix viscosity is sufficiently low to allow pouring of the composite mixture into a mold or rocket motor.^{37,43} While the preparation of CPs is different than some PBXs, many of the same formulation-mechanical property relationships exist. However, the ignition behavior of CPs are much different than PBXs as they are designed for a different application.

1.3.1 Mechanical Properties

As mentioned above, the effect of strain-rate, temperature, and particle size on the mechanical properties of CPs are similar to their effect on PBXs. For one, as strain rate increases⁴⁴⁻⁴⁶ and temperature decreases,⁴⁵⁻⁴⁷ the strength and modulus of HTPB-based CPs increase. Additionally, in an HTPB-RDX-Al PBX where HTPB was present at 15% (by weight), as the particle size of aluminum was decreased from 860-1680 μm to 120-250 μm , the compressive strength of the composite increased from 9.82 kg cm^{-2} to 13.83 kg cm^{-2} .⁴⁸ While these results are from a PBX, they are representative of common HTPB-AP-Al CPs, as the composition is similar to commonly used CP formulations. Thus, the strengthening effect observed in PBXs when decreasing particle size is also seen in CP formulations. Together, the dependence of CP's

mechanical properties on strain rate, temperature, and particle size reveal that CPs exhibit similar mechanical behavior to PBXs.

1.3.2 Effect of Temperature on Ignition Behavior

While the mechanical property considerations of CPs are similar to PBXs, the combustion behavior is different. That is, PBX are designed to detonate and CPs are designed to burn, produce hot gases, and generate thrust.^{1,3} Whereas temperature and particle size effects the sensitivity of PBXs in transitioning to detonation, these variables effect the burn rate of CPs. As the initial temperature of AP-based CP grains increase, the burn rate also increases.^{49,50} Additionally, as the particle size of AP decreases, the burn rate increases.⁵¹

Even though CPs are designed to resist detonating when exposed to unwanted impact or shock impulses, there are instances when these propellants transition to detonation and rapidly release their chemical energy.⁵²⁻⁵⁴ To investigate the effect of temperature on a CP's tendency to transition to detonation, shock sensitivity experiments at ambient and elevated temperatures were performed on a CP composed of 73% (by weight) AP, 15% Al, and 12% carboxy terminated polybutadiene (CTPB) as the binder. In these experiments, the shock sensitivity of the CP was nearly identical at ambient temperature and 170 °C.⁵⁴ Furthermore, it has been demonstrated that an elastomer modified cast double-base propellant (EMCDBP) has a reduced sensitivity to impact ignition when it is heated above the glass transition temperature of the elastomer.⁵⁵ An EMCDBP is another type of solid propellant, a cast double-base propellant, with a polymer binder added to improve its mechanical properties.³⁷ While it might be expected that a solid propellant's sensitivity to detonation would increase with increasing temperature, these shock and impact sensitivity results demonstrate the complex temperature-sensitivity relationship present in solid propellants that contain polymer binders.

1.4 Summary of Energetic Composites

The mechanical properties and sensitivity of energetic composites are influenced by a variety of factors, with the polymer binder having an outsized influence on these properties given its relatively low weight percentage. In both PBXs and CPs, the binder serves to improve the mechanical integrity and decrease the sensitivity of the composites. Furthermore, the combustion

behavior of PBXs and CPs is highly dependent on temperature. Therefore, the ability to modulate the temperature of these energetic composites in real time could provide a way to adjust the performance of these materials on demand. If a composite energetic material was electrically conductive, it could be heated by Joule heating, thus providing a method to modulate its temperature on demand. With an understanding of the mechanical properties of PBXs and CPs, it becomes possible to utilize electrically conductive polymers as binders to confer conductivity to the composites while retaining favorable mechanical properties.

1.5 Electrically Conductive Polymers

Traditionally, polymers are electrically insulating, stifling the flow of electrons. However, in recent years, polymers with electrical conductivity have been realized and the emergence of these conductive polymers brings about the possibility of producing conductive energetic composites. There are two broad classes of polymers capable of conducting electrons, conjugated polymers and radical polymers. The most widely studied are conjugated polymers, which have a large degree of conjugation in their macromolecular backbone.⁵⁶⁻⁵⁹ Alternatively, radical polymers have recently been found to be electrically conductive and their utility in organic electronics is being explored by several researchers.⁵⁹⁻⁶⁸ As conjugated polymers have been the subject of many research efforts, their mechanical properties have been thoroughly investigated.⁶⁹⁻⁷⁴ On the other hand, the mechanical properties of radical polymers have not been examined. In the following sections, the mechanical properties of conjugated polymers will be discussed along with their potential application as binders in energetic materials. Furthermore, radical polymers will be introduced and their potential advantages as binders in composite energetics will be considered.

1.5.1 Conjugated Polymers

Conjugated polymers are a class of polymers that have alternating single and double bonds in their macromolecular backbone.^{56,57} In their pristine state, these polymers can exhibit either insulating or semiconducting behavior.⁵⁷ Once a conjugated polymer is reduced or oxidized with a dopant, electrons are added to or taken from the polymer, respectively. This results in the polymer having an excess of electrons or a deficiency of electrons (holes) in the conjugated system, giving the polymer charge carriers that enable the conduction of electrons.^{56-58,75} The large amount of π

bonds present in conjugated polymers allow these charge carriers to delocalize and move through the polymer.⁵⁷ The sp^2 hybridization of carbon atoms in the polymer backbone allows for charge transport but also causes stiffness in conjugated polymers.⁷⁶ For this reason, conjugated polymers are generally mechanically stiff. This characteristic of conjugated polymers could limit their use as binders in composite energetics. Specifically, PBXs generally utilize compliant binders to reduce the sensitivity of the high explosive and CPs employ compliant binders to enable cast-curing and allow for high strain tolerances.⁷⁷

Much of the research concerning the mechanical properties of conjugated polymers has been done with thin films due to their widespread use in solar cells, transistors, and other devices in thin film form.⁷¹ A widely used technique for determining the tensile modulus of polymer thin films is the buckling instability technique. This method has been used to measure Young's moduli of polymer thin films in agreement with the moduli of bulk polymers. However, when film thicknesses fall below 40 nm, Young's moduli measured by the buckling instability technique have been observed to deviate from the moduli measured from bulk polymer samples.⁷⁸ In the studies discussed below, all the polymer films measured were greater than 50 nm in thickness. Thus, a discussion concerning the mechanical properties of conjugated polymer thin films and their utility as binders in composite energetic materials is valid and useful.

The stiff mechanical behavior of highly conjugated polymers is demonstrated by a study that investigated the mechanical properties of over 40 low bandgap conjugated polymers by the buckling instability technique. In this work, the authors found that the tensile modulus of the polymers were between 0.150 GPa and 3.79 GPa.⁷² For reference, HTPB, the thermoset elastomer used extensively as a CP binder, has a tensile modulus between 0.05 and 3.10 MPa.^{79,80} Thus, the low bandgap conjugated polymers had stiffnesses 2-5 orders of magnitude greater than HTPB. Furthermore, the authors observed that polymers containing fused rings in their backbone had higher tensile moduli than polymers with isolated rings in their main chain. Additionally, they found that polymers with branching side chains had lower stiffnesses, which they attributed to a likely decrease in crystallinity that resulted from reduced packing efficiency of polymer chains.⁷² This is an expected result, as conjugated polymers with longer side groups have been reported to have lower tensile moduli in other works, as well. When the length of the side chain in poly(3-alkylthiophene) (P3AT) was increased from 4 to 8 carbon atoms, the tensile modulus decreased

from 1.87 GPa to 0.15 GPa.⁷³ Thus, it has been demonstrated that larger side groups in conjugated polymers decreases their stiffness.

While decreasing the number of fused rings in the backbone and increasing the size of side groups decreases the stiffness of conjugated polymers, increasing molecular weight of conjugated polymers increases their ductility. As measured by the buckling instability technique, the crack onset strain of poly(3-hexylthiophene) (P3HT) increased from 2.83% to 31.17% when the molecular weight increased from 15 to 80 kg mol⁻¹.⁷¹ In a separate study, when bulk P3HT samples were tested, the elongation at break increased from ~25% to ~300% when the molecular weight increased from 25 to 90 kg mol⁻¹.⁸¹ Therefore, it has been demonstrated that increasing the molecular weight of polythiophene-based conjugated polymers increases their ability to deform plastically.

An important factor contributing to the conductivity of conjugated polymers is their crystallinity. Crystallinity in conjugated polymers has been demonstrated to increase their conductivity. In solar cells containing P3HT, a widely used conjugated polymer, the charge transport was improved by thermally annealing the cells, which was attributed to increased crystallinity in the P3HT component of the solar cells.⁸² Furthermore, the conductivity of poly(3-octylthiophene) (P3OT), a polymer with a similar structure to P3HT, increased from 15 S cm⁻¹ to 40 S cm⁻¹ when the percent crystallinity of the polymer increased from 3% to 14%.⁷⁵ Moreover, the mechanical properties and field effect mobility of two polymers, P3HT and poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT), a conjugated copolymer, were investigated. It was found that in these chemically similar polymers, as the tensile modulus increased, the field effect mobility increased as well. Furthermore, these two characteristics both increased with increasing crystallinity. Thus, it was demonstrated that not only does crystallinity improve the charge transport in conjugated polymers, but it also increases the stiffness of these polymers.⁸³

Many research efforts have focused on understanding the structure-mechanical property relationships in conjugated polymers. Meanwhile, other researchers have physically mixed conjugated polymers with other molecules to enhance their mechanical properties. A striking example of this approach is the addition of Zonyl, a plasticizer, to poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) to dramatically increase its compliance. PEDOT:PSS is a conjugated polymer, PEDOT, doped with the polyelectrolyte PSS and is a commonly used conjugated polymer that is known to be very stiff and

brittle. When prepared in a solution of 5% (by weight) DMSO, the tensile modulus of PEDOT:PSS was found to decrease from 7.49 GPa to 0.03 GPa when the Zonyl concentration increased from 0.1% to 10% (by weight). Importantly, the polymer maintained its high electrical performance as the stiffness dramatically decreased.⁷⁴ Therefore, this result demonstrates that the high stiffness of conjugated polymers can be decreased by the addition of small molecules.

While different strategies have been shown to increase the compliance and ductility of conjugated polymers, the mechanism by which they conduct charge biases them towards stiff, brittle behavior. The stiffness of conjugated polymers could be a barrier to using them as binders for energetic composites because binders used for PBXs and CPs are generally much more compliant. Adjusting the molecular structure or adding plasticizing molecules to conjugated polymers are strategies that could result in conductive polymers being compliant enough for use in energetic composites. Another strategy to achieve both compliance and electrical conductivity is to utilize polymers that can conduct charge by a mechanism that is not dependent on the stiff, inflexible π bonds present in conjugated polymers.

1.5.2 Radical Polymers

In contrast to conjugated polymers, radical polymers lack conjugation in their main chain and possess substituents that contain stable radicals.^{59,62} These stable radicals are long-lived due to stabilization arising from highly conjugated or sterically bulky side groups.⁵⁹ The unpaired electrons in radical polymers allow for oxidation-reduction (redox) self-exchange reactions, enabling charge transport in the solid state.^{59,62} An increasing interest in radical polymers in recent years has resulted in the discovery of multiple polymers that possess electrical conductivities between 10^{-4} and 10^{-6} S cm⁻¹.^{63,66,84,85} Furthermore, the radical polymer with the highest reported electrical conductivity, poly(4-glycidyoxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO), has been demonstrated to have a conductivity of ~ 0.1 S cm⁻¹ at length scales less than 600 nm.^{60,65} Because of their relatively recent introduction to the academic research landscape, the mechanical properties of radical polymers have not yet been explored. However, because the conductivity of radical polymers is not dependent on rigid π bonds in their main chain, they present an opportunity to develop polymers that are both conductive and compliant. In this way, radical polymers could provide a means to imparting electrical conductivity to energetic composite materials, while retaining the favorable mechanical and sensitivity properties observed in traditional PBXs and CPs.

While the mechanical properties of radical polymers have not been investigated, recent studies on the electrical properties of novel radical polymers give insight on potential structure-mechanical property relationships in these polymers. For example, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), has a modest electrical conductivity of 10^{-6} S cm^{-1} with a T_g of ~ 170 °C.⁶³ PTEO, whose structure is very similar to PTMA, demonstrated the record breaking conductivity for a radical polymer of ~ 0.1 S cm^{-1} , with a T_g of ~ 20 °C.⁶⁵ The much higher conductivity of PTEO compared to PTMA is attributed to the increased chain mobility of PTEO which allows for chain reorganization and formation of radical networks upon thermal annealing.⁶⁵ In other words, the increased electrical performance is associated with a softening (decreased T_g) of PTEO compared to PTMA. This is in contrast to conjugated polymers, where crystallization and hardening of the polymers tend to correlate with an increase in charge carrier mobility.^{75,76,82,83} Furthermore, poly[2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-(λ 1-oxidaneyl)phenyl)(4-((3-(methoxydimethylsilyl)propoxy) methyl)phenyl)methylene)cyclo-hexa-2,5-dien-1-one] (PGMS), a radical polymer with a T_g of -20 °C, achieved a solid state conductivity of 10^{-4} S cm^{-1} .⁶⁶ The conductivity of PGMS likely did not reach the level of PTEO due to low radical content in the polymer.⁶⁶ Still, this result further demonstrates that improvements in the conductivity of radical polymers can be made while simultaneously softening the polymers. Because polymer binders for energetic composites are often soft and compliant, the ability to improve the electrical performance of radical polymers while simultaneously lowering their T_g makes them attractive for this application. Mechanical characterization of candidate radical polymer binders is still needed. However, studies concerning the electrical properties of radical polymers are promising in terms of their potential for concurrent optimization of their electrical and mechanical performance for composite energetic binder applications.

1.6 Summary

PBXs and CPs are two classes of energetic materials that utilize polymers as binders to improve the mechanical, sensitivity, and processing properties of the composites. While many factors contribute to the final mechanical properties and sensitivity of PBXs and CPs, the binder has a significant influence on these characteristics. Typically, the polymer used as the binder is compliant enough to desensitize the energetic material and to improve the ease of processing. Meanwhile, conjugated polymers, the most widely studied and high performing electrically

conducting polymers, exhibit stiff and brittle behavior due to the high number of π bonds in their main chain. Therefore, to confer electrical conductivity to energetic composites using conductive binders, the stiffness of conductive polymers must be addressed. There have been research efforts devoted to increasing the compliance of conjugated polymers by modifying their structure and mixing them with other molecules. Another strategy for decreasing the stiffness of conductive polymers for use as binders in energetic materials is to utilize polymers that are not dependent on extensive conjugation in their main chain to conduct charge. Radical polymers transport charge through a mechanism not involving main chain conjugation, thereby presenting an opportunity to achieve compliance and conductivity in polymers. Thus, radical polymers could present alternative binders for energetic composites that contain the same compliance of traditional binders, but also offer electrical conductivity to the final energetic material.

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2. FIRST STEP TOWARD A RADICAL POLYMER-BASED CONDUCTIVE ENERGETIC MATERIAL

2.1 Introduction

Plastic bonded explosives (PBXs) and composite propellants (CPs) utilize polymeric species to improve the processability and mechanical properties of high explosives and solid propellants. PBXs and CPs are composed of a high proportion (i.e., 80-95%, by weight) of energetic material distributed in a polymeric matrix.¹⁻⁴ Since the conception of PBXs and CPs in the 1940s and 1950s,^{2,4} polymeric materials have advanced significantly on many fronts, including their ability to be electrically conducting.^{5,6} Polymers with electrical conductivities in excess of 10^4 S cm^{-1} have been developed,⁷ and the majority of the effort to develop these polymers have focused on π -conjugated polymers.⁵⁻⁹ Despite the promising properties that have been developed for a range of polymer conductor systems, there has been little effort to use these polymers as the binder phase of PBXs or CPs to confer electrical conductivity to the composites.

On the other hand, researchers have evaluated carbon nanotubes (CNTs) as a means by which to confer electrical conductivity to PBXs and CPs for the application of real-time damage sensing in energetic materials.¹⁰⁻¹² While impressive performance was seen, practicality aspects, especially at the large scales required, limit the potential translation of CNT-polymer composite systems in practical applications.¹³ On the other hand, there are other applications that have yet to be examined. Specifically, leveraging the resistive heating ability of such a conductive energetic composite has yet to be reported. The ability to heat PBXs or solid propellants on demand with an electrical stimulus could provide greater control of the performance of these materials. For instance, the burn rate of a solid propellant generally increases with increasing initial propellant temperature,¹⁴⁻¹⁸ and modulating the temperature of a solid propellant electronically could provide on-demand control of the burn rate. Additionally, heating a solid propellant affects its sensitivity to detonation by shock impulse. In some cases, heating a propellant will decrease its sensitivity to shocks,¹⁹⁻²¹ and in other cases it will increase its sensitivity to shocks.²¹ Thus, it is straightforward to envision different instances where it would be useful to increase or decrease the likelihood of a propellant exploding when exposed to a shock impulse. Furthermore, using an electric signal to resistively heat a PBX could sensitize the explosive to shock or mechanical impulse. Researchers have demonstrated an increase in shock sensitivity in PBXs containing 1,3,5,7-tetranitro-1,3,5,7-

tetrazacyclooctane (HMX)^{22,23} and 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) when heated.²⁴ Alternatively, Zhao et al. revealed that a 1,3,5-trinitro-1,3,5-triazine (RDX) based PBX containing 30% (by weight) aluminum had a decreased shock sensitivity with increasing temperature up to 110 °C and an increased shock sensitivity with increased temperature above 110 °C.²⁵ Given an understanding of the sensitivity of a PBX as temperature changes, the ability to heat such an explosive with an electrical signal could provide useful in modulating its detonation behavior.

Though conjugated polymers have demonstrated the highest electrical conductivities among conducting polymers, their chemical structure could limit their usefulness as a binder in PBXs and solid propellants. Specifically, the large degree of π -conjugation necessary for charge conduction often produces brittle polymers, and this could limit their usefulness as binders for low sensitivity PBXs.^{8,26-31} Another class of conducting polymers, radical polymers, can be designed to have more robust mechanical properties relative to their conjugated polymer counterparts. Here, radical polymers lack conjugation in their backbone and carry pendant groups that contain open-shell species. These radicals can undergo rapid reduction-oxidation (redox) reactions, enabling them to conduct charge in the solid state.^{9,32-39} These polymers are not dependent on rigid macromolecular design motifs to conduct charge. Therefore, radical polymers have the potential to be both electrically conductive and sufficiently compliant to serve as a desensitizing binder.⁴⁰

The radical polymer with the highest reported electrical conductivity ($\sim 10 \text{ S m}^{-1}$) is poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO).^{36,38} PTEO is a polymer consisting of a poly(ethylene oxide)-like (PEO-like) backbone with pendant 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) radicals.^{36,38} This conductivity was achieved up to distances of 600 nm, after which the conductivity decreased precipitously.³⁶ Therefore, to confer electrical conductivity to a PBX using PTEO as a binder, a strategy to address macroscale conductivity is needed. Another important consideration in composite energetic materials is crosslink density in the binder. PBXs^{41,42} and CPs⁴³ both contain crosslinks of some kind which have a rigidizing effect on the composite. PTEO does not contain substituents that could initiate crosslinking reactions. Thus, the addition of a crosslinker to PTEO would give greater control of the final mechanical properties of a PTEO-based composite.

Here, a nanocomposite design strategy has been implemented to confer electrical conductivity to a mock-PBX material. The composite material was composed of 90% solid particles to simulate the mechanical properties of common explosive crystals. PTEO and an

ultraviolet-crosslinkable (UV-crosslinkable) copolymer based on PTEO were used as the polymeric binders. Lastly, low loadings of silver nanowires (AgNWs) were added to connect electrically conducting domains of PTEO. The viscoelastic response of the polymer and composites were measured by dynamic mechanical analysis (DMA) which revealed that the PTEO-based composites performed similarly to a common PBX, namely PBX 9502. The crosslinker added to PTEO and the AgNWs had a similar effect on the viscoelastic response of the composites. Specifically, they increased the stiffness and decreased damping in the material. The electrical conductivity values of the composites were also quantified as a function of AgNW content, which showed that meaningful conductivities ($\sim 1 \text{ S cm}^{-1}$) could be achieved at AgNW loadings $< 3\%$ (by weight). Thus, the materials system presented here provides a method for imparting electrical conductivity to PBXs that could be used in designing composites capable of direct resistive heating.

2.2 Experimental

2.2.1 Materials

All of the chemicals were purchased from Sigma-Aldrich, and they were used as received unless stated otherwise. Silver nanowires (AgNWs) were purchased from ACS Materials as a suspension in isopropanol (IPA) with an average diameter of 30 nm and a typical length of 100-200 μm . Sugar crystals used were sieved to obtain an average particle diameter of $\sim 150 \mu\text{m}$.

2.2.2 General Methods

Differential scanning calorimetry (DSC) thermograms of PTEO and PTEO-co-glycidyloxybenzophenone (PTEO-GBP) were obtained using a TA Instruments Q20 differential scanning calorimeter under a nitrogen atmosphere with a flow rate of 50 mL min^{-1} . All of the experiments consisted of an initial heating to $150 \text{ }^{\circ}\text{C}$, an isothermal hold for 10 minutes, cooling to $-50 \text{ }^{\circ}\text{C}$, and another heating to $150 \text{ }^{\circ}\text{C}$ and cooling to $-50 \text{ }^{\circ}\text{C}$. The heating and cooling rates were both $10 \text{ }^{\circ}\text{C min}^{-1}$, and the data presented are of the second heating scans. Proton (^1H) nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance III 400 MHz HD spectrometer. All of the samples were dissolved in deuterated dimethyl sulfoxide. PTEO homopolymer spectra were obtained by quenching nitroxide radicals with phenyl hydrazine.

PTEO-GBP copolymer spectra were obtained by quenching the nitroxide radicals through an overnight reaction of hydrochloric acid and the polymer in a chloroform/methanol solution. The fraction of GBP repeat units in the PTEO-GBP copolymers were determined by integrating the methyl peaks from the nitroxide groups and the aromatic peaks from the benzophenone groups. Fourier transform infrared (FTIR) spectra were obtained using a Thermo Scientific Nicolet Nexus FT-IR spectrometer. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMX EPR spectrometer. Solutions for EPR measurements contained 1 mg mL⁻¹ PTEO or PTEO-GBP in chloroform. Molecular weights of the polymers were determined by size exclusion chromatography (SEC) using a Hewlett-Packard 1260 Infinity series with a Hewlett-Packard G1362A refractive index detector and three PLgel 5 μ m MIXED-C columns. Polystyrene (PS) standards (Agilent Easi Cal) from 1-200 kg mol⁻¹ were used to calibrate the instrument. Tetrahydrofuran was used as the mobile phase with a temperature of 35 °C and a flow rate of 1 mL min⁻¹.

2.2.3 Synthesis

The radical containing monomer, 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEO), was synthesized according to a procedure modified from the literature.³⁶ In an example reaction, epichlorohydrin (10 mL, 0.120 mol) and tetrabutylammonium hydrogen sulfate (1.5 g, 0.0046 mol) were added to an aqueous sodium hydroxide solution (50% NaOH by weight, 16 g total). A solution of 4.0 g (0.023 mol) of 4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO-OH) dissolved in ~30 mL of THF was then added dropwise to the aqueous solution. The mixture was stirred for 16 h. After 16 h, ~200 mL of water was poured into the reaction mixture. It was extracted with ethyl acetate, washed with water and brine, and dried with anhydrous magnesium sulfate. The ethyl acetate was removed by rotary evaporation and the product was then purified in a silica gel chromatography column with an 8:1 (v/v) hexanes:ethyl acetate eluent. The eluent was removed from the monomer in a vacuum oven over 24 h, and the monomer was recovered as needle-shaped red crystals.

The crosslinkable co-monomer, glycidyloxy-benzophenone (GBP), was synthesized according to a procedure modified from the literature.⁴⁴ Sodium hydroxide (1 g, 0.025 mol) was dissolved in epichlorohydrin (25 mL, 0.30 mol) and 4-hydroxybenzophenone (3 g, 0.015 mol) was added to the solution. The mixture was refluxed at 120 °C for 5 h and then stirred overnight at

room temperature. The product was extracted with ethyl acetate, washed with water and brine, and dried with magnesium sulfate. The MgSO_4 was removed by gravity filtration and the ethyl acetate was removed by rotary evaporation to yield an oily, clear liquid. The liquid was placed in a vacuum oven overnight to yield a white solid.

PTEO and the copolymer, PTEO-*co*-GBP (PTEO-GBP), were synthesized according to procedures modified from the literature.^{36,45} An example reaction for the synthesis of PTEO-GBP is as follows. In an inert atmosphere, 910 mg of TEO, 90 mg of GBP, 226 mg of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), and a solution of 32 mg of potassium *tert*-butoxide in 0.6 mL of inhibitor free tetrahydrofuran was added to a glass vial. The mixture was stirred for 24 h at 40 °C in the inert atmosphere. The reaction mixture was then exposed to air, dissolved in dichloromethane, washed with water and brine, and dried with magnesium sulfate. The magnesium sulfate was filtered using gravity filtration, and the dichloromethane was removed by rotary evaporation. The red, viscous liquid remaining was dissolved in minimal amount of tetrahydrofuran and added dropwise to an excess of hexanes. The red, viscous polymer precipitated to the bottom of the container. The hexanes were decanted, and the polymer was collected. The amount of GBP added to the reaction mixture was varied to achieve different GBP loadings in the polymer.

2.2.4 Mock PBX Formulation

Mock PBX molding powder was produced by a solvent-antisolvent method. Sugar was suspended in hexanes by vigorous stirring. For the formulation of composites composed of only polymer and sugar, a solution of PTEO or PTEO-GBP with a concentration of 100 mg mL⁻¹ in chloroform was added to the sugar suspension. The polymer precipitated from solution to coat the sugar particles. The suspension was stirred for ~5 additional min. The hexanes were then decanted, and the sugar-polymer composite powder was collected. For the formulation of composites composed of PTEO or PTEO-GBP, sugar, and AgNWs, the same procedure was followed with a minor adjustment. A specified volume (AgNW desired loading) of AgNW suspension in IPA was added to the polymer solution and stirred. This combined polymer-AgNW suspension was then added to the sugar suspension. The PTEO-sugar-AgNW molding powder was collected after decanting the hexanes.

The molding powder was pressed into samples for dynamic mechanical analysis (DMA) and conductivity testing. First, a 30 mm $\times$ 7 mm $\times$ 0.7 mm rectangular Teflon mold was filled with molding powder. Then, a piece of Teflon film (McMaster-Carr) was placed over the powder and pressed in a hydraulic press at 100 °C with 1,000 lbs of force. This position was held for 15 min. After 15 min the force was reestablished to 1000 lbs. if it had lessened, and held for 15 more min, for a total of 30 min in the press. These samples were then heated for an additional 3 h at 100 °C in a vacuum oven. If the sample was also cured with ultraviolet (UV) light, it was placed under a 36 W UV lamp for 6 h. Halfway through the UV cure, samples were turned to expose the opposite side to the lamp. For DMA testing, the entire 30 mm $\times$ 7 mm $\times$ 0.7 mm sample was used. For conductivity testing, the samples were gently heated and cut into small rectangles ~5-10 mm long.

2.2.5 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) experiments were performed using a TA Instruments Q800 instrument, with a 17.5 mm single cantilever clamp. Temperature sweep experiments were conducted at a frequency of 1 Hz, an amplitude of 10 μ m, and a heating rate of 1 °C min⁻¹. Frequency sweep experiments were conducted at 25 °C, a soak time of 10 min, and an amplitude of 10 μ m. All of the samples were secured in the clamps using 1 in-lb of torque, as measured by a torque screwdriver. Exact dimensions of rectangular DMA samples were measured with calipers for the calculation of storage moduli and loss moduli. Neat polymer samples were prepared in the same manner as the PTEO-sugar composites. The rectangular Teflon molds discussed previously were filled with polymer, pressed at 100 °C, and heated for another 3 h at 100 °C under vacuum. If the sample received UV treatment, it was processed in the same manner as described above.

2.2.6 Electrical Conductivity Testing

The electrical conductivity of the materials was measured using a Keithley 2400 source meter. Electrical leads outfitted with flat alligator clips were attached to rectangular specimens and the resistance was measured with the source meter. The resistance along with the dimensions of the rectangular piece of material was used to calculate volume conductivities of the composites.

2.3 Results and Discussion

The polymer binders used in this study were homopolymer PTEO and the random copolymer poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-co-glycidyloxybenzophenone) (PTEO-GBP) (Figure 2.S1). The molecular structures and molecular weights of the PTEO and PTEO-GBP used in this work were characterized using ^1H NMR spectroscopy, FTIR spectroscopy, EPR spectroscopy, and SEC (Figure 2.S2-2.S7), and the data reported here is consistent with previous reports of these polymeric species.^{38,46,47} As mentioned previously, PTEO was chosen for its best-in-class conductivity. On the other hand, PTEO-GBP was designed to retain the conductivity of PTEO while providing a handle by which to tune the mechanical properties of the macromolecule, as the GBP unit can be crosslinked through simple exposure to ultraviolet light.^{34,48-50} When benzophenone undergoes a UV-initiated reaction, it forms a benzopinacol or alkylbenzhydrol species in PTEO-GBP (Figure 2.1a).⁵⁰ This is evidenced by the increased intensity of the alcohol stretch in the FTIR spectrum of PTEO-GBP after UV exposure (Figure 2.1b).

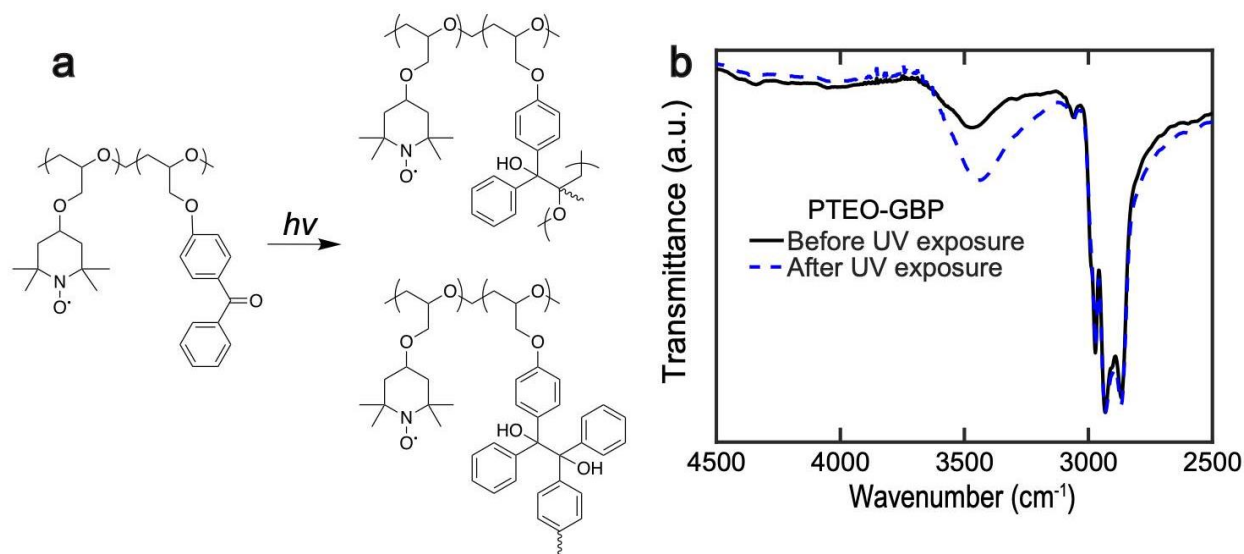


Figure 2.1. (a) PTEO-GBP before (left) and after (right) UV crosslinking. PTEO-GBP can either form an alkylbenzhydrol (top) or benzopinacol species (bottom). Wavy lines represent the rest of the polymer not shown in the crosslinked structures. (b) FTIR spectra of PTEO-GBP before and after UV exposure. An increase in the intensity of the alcohol stretch at $\sim 3400\text{ cm}^{-1}$ indicates that UV crosslinking forms alcohol groups.

DSC scans of PTEO and PTEO-GBP reveal that, before thermal annealing, PTEO-GBP has a reduced glass transition temperature (T_g) relative to PTEO (Figure 2.2a). After thermal annealing, PTEO-GBP(8.5) has a similar T_g to PTEO and PTEO-GBP(16.3) has an increased T_g relative to PTEO (Figure 2.2b). The T_g of PTEO was ~ 20 °C, and this agrees with previous studies.^{36,38} After thermal treatment, PTEO does not exhibit an appreciable change in its T_g , as expected. These results suggest that the GBP moiety within the PTEO-GBP copolymer acts as a means by which to lower the glass transition temperature of the copolymer. After thermal annealing, this effect of benzophenone substituents is no longer present, which is consistent with intuition. If enough GBP is present in the polymer, the T_g of the copolymer is increased to a higher temperature than what is observed for PTEO.

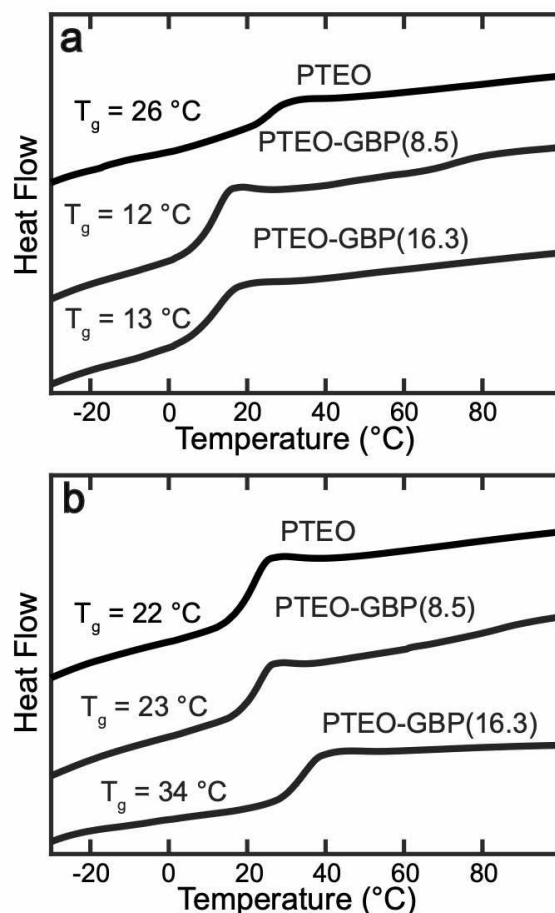


Figure 2.2. DSC thermograms of PTEO and PTEO-GBP (a) before and (b) after thermal treatment. Before thermal treatment, PTEO-GBP has a reduced T_g compared to PTEO. After thermal treatment, its T_g increases to a similar or higher temperature compared to PTEO. PTEO-GBP(X) signifies a polymer with X% GBP, on a molar basis. Endotherms are displayed in the upward direction.

DMA experiments on neat polymer samples without UV crosslinking revealed that PTEO-GBP copolymers behave more elastically than PTEO (Figure 2.3). In this case, all of the samples were subjected to the hot press and a 3-h thermal curing process. After thermally treating the polymers, we observed an increase in the storage modulus (E') in the glassy region for the PTEO-GBP copolymers (Figure 2.3a). E' is a measure of the amount of energy stored elastically in a material, so an increase in this parameter demonstrates PTEO-GBP is more rigid than PTEO.⁵¹ The loss modulus (E'') is also higher across all of the temperatures in the copolymer (Figure 2.3b) aside for the case of PTEO-GBP(12.6). E'' is a measure of energy loss due to internal motions of polymer chains.⁵² The higher E'' in PTEO-GBP suggests PTEO-GBP chains require more energy

to induce chain slippage than PTEO. Further demonstrating that PTEO-GBP behaves more elastically than PTEO, the $\tan \delta$ values across most temperatures are reduced for PTEO-GBP (Figure 2.3c). Because $\tan \delta$ is a ratio of the viscous response (E'') to the elastic response (E'),⁵¹ the higher damping values for PTEO show that it exhibits more viscous behavior than PTEO-GBP.

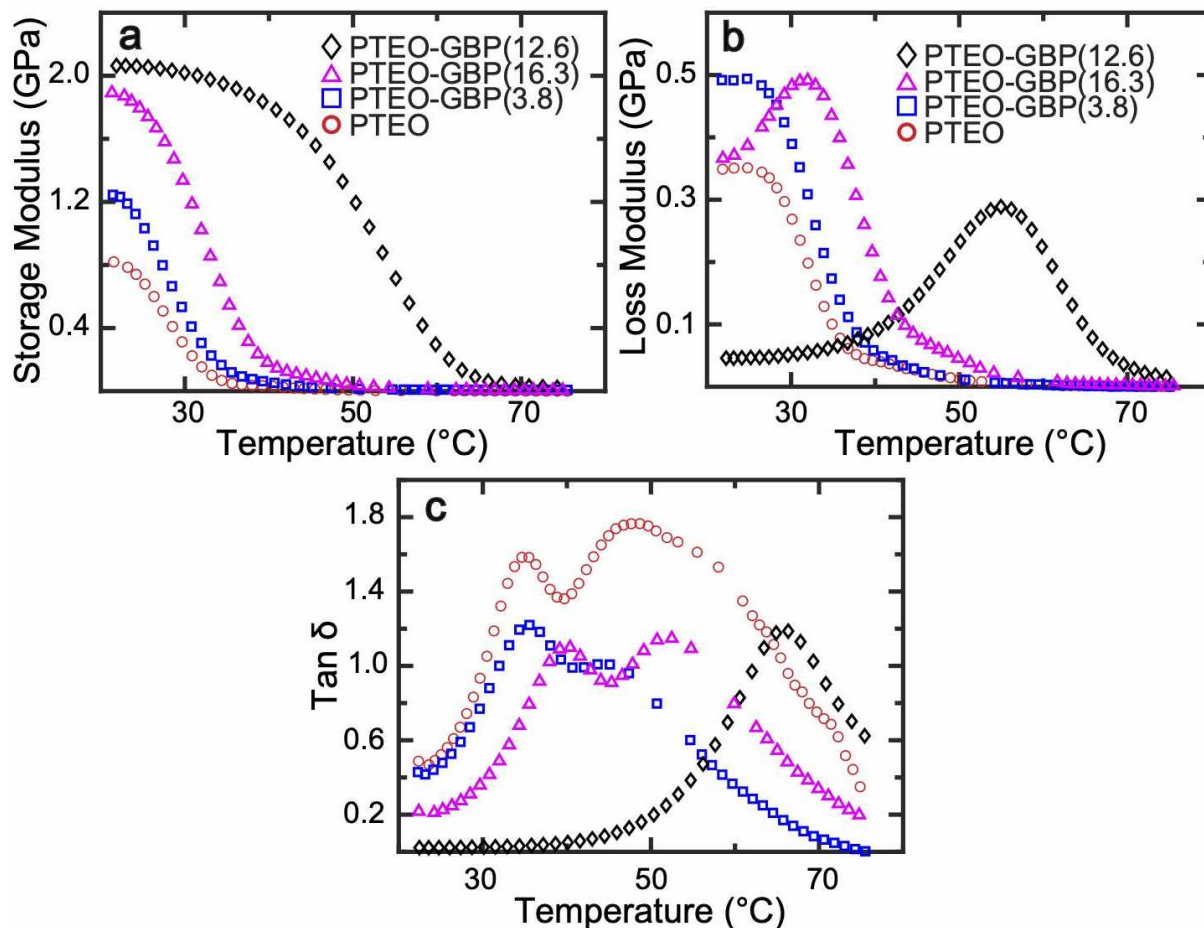


Figure 2.3. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ versus temperature for thermally treated neat polymer samples. PTEO-GBP(X) indicates a copolymer with X% GBP, on a molar basis.

Like the DSC experiments, the DMA results show that the T_g of PTEO-GBP after thermal treatment is higher than the T_g of PTEO when the copolymer has a large content ($\sim 15\%$) of GPB. This is demonstrated by the first $\tan \delta$ peak in PTEO-GBP(16.3) occurring at 40 °C compared to 35 °C for PTEO. The second peak in the PTEO and PTEO-GBP(3.8) samples are likely an artifact of the samples exiting the sensitivity range of the DMA Q800. As McAninch et al. point out, the

TA Instruments Q800 accurately measures samples with stiffnesses between 10^2 and 10^7 N/m.⁵³ The PTEO and PTEO-GBP(3.8) samples fall below 100 N m^{-1} at 39°C and 47°C , respectively. Therefore, the second $\tan \delta$ peaks for PTEO and PTEO-GBP(3.8) were generated outside of the sensitivity limits of the instrument and should not be considered valid. On the other hand, PTEO-GBP(16.3)'s stiffness does not fall below 100 N m^{-1} until 62°C . Therefore, the second $\tan \delta$ peak in PTEO-GBP(16.3) was observed within the sensitivity limits of the instrument (Figure 2.3c). At higher proportions of GBP in the copolymer ($>15\%$), PTEO-GBP appears to exhibit multiple glass transitions. Two glass transitions were observed from the $\tan \delta$ curve and not the DSC thermograms (Figure 2.2) of PTEO-GBP(16.3) due to the much greater sensitivity of DMA in observing polymer transitions.⁵⁴ Furthermore, the DSC thermogram of PTEO-GBP(19.3) appears to reveal two glass transitions (Figure 2.S8). Random copolymers exhibiting multiple glass transitions has been observed previously. Estane 5703, a poly(ester urethane) random copolymer used as the binder in PBX 9501,⁵⁵ displays two $\tan \delta$ peaks.⁴² Estane exhibits phase separation between hard and soft components,^{41,42} and the two $\tan \delta$ peaks are associated with separate glass transitions of hard and soft segments of the polymer.⁴² The much higher T_g of PTEO-GBP(12.6) is not caused by the GBP portion of the copolymer. Instead, PTEO-GBP(12.6) had an anomalous molecular weight distribution. A significant portion of the polymer had a larger molecular weight than other polymers (Figure 2.S7), which likely accounts for the much higher T_g .

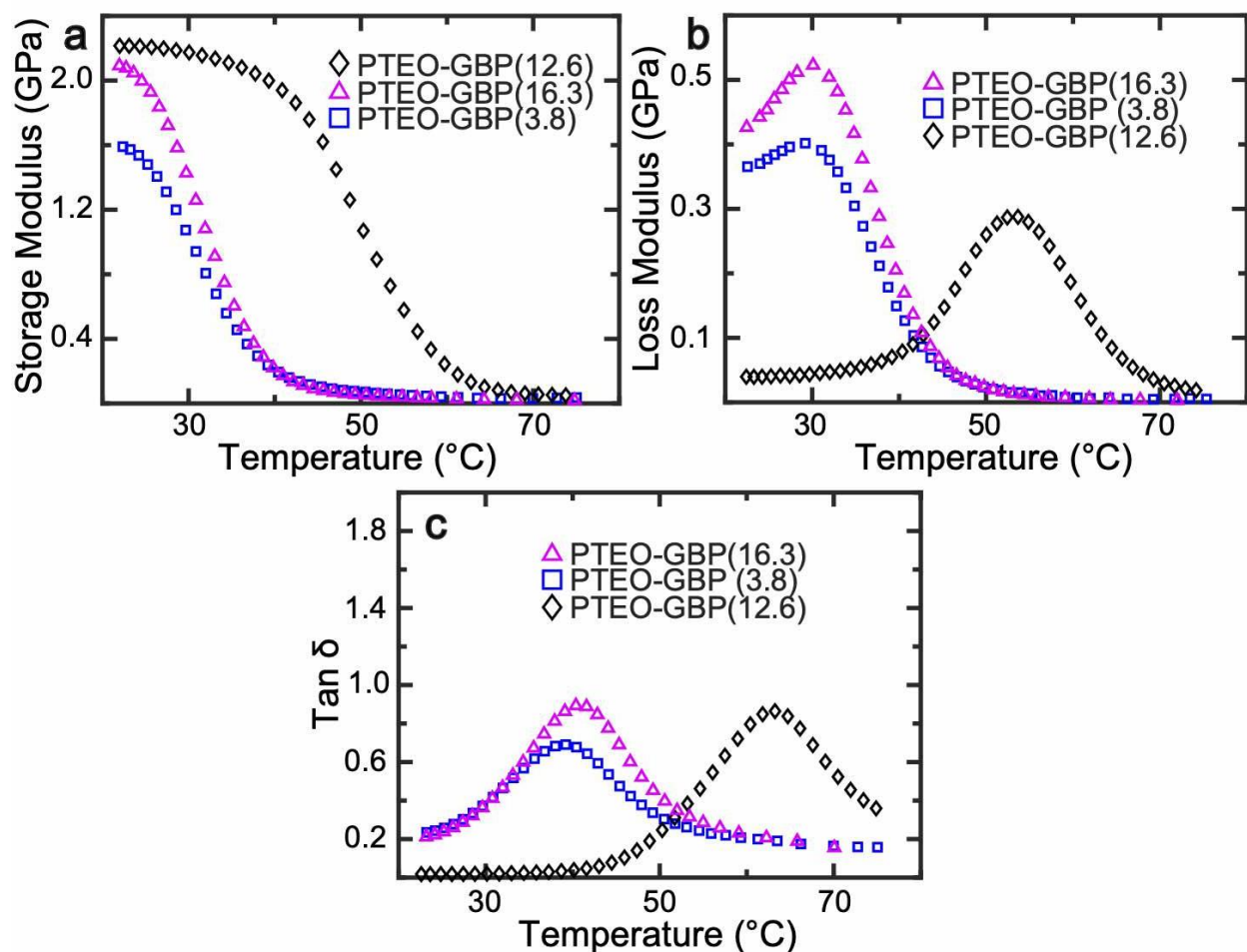


Figure 2.4. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ vs temperature for UV-treated neat polymer samples. PTEO-GBP(X) indicates a copolymer with X% GBP, on a molar basis.

Each of the PTEO-GBP copolymers showed evidence of crosslinking after being exposed to UV light (Figure 2.4). The glassy and rubbery E' increased for each polymer after being cured with UV light (Figure 2.4a). An increase in the rubbery E' is especially indicative of crosslinking, as covalent crosslinks remain intact through the T_g . In contrast to the samples that did not receive UV treatment, the stiffness of the UV treated samples remained above the lower sensitivity limit (100 N m^{-1}) well into the rubbery region. Additionally, damping decreased across all of the temperatures for each of the samples, indicating an increase in elasticity (Figure 2.4c). Furthermore, the plot of E'' versus temperature gives insight into the relative percentage of crosslinking units consumed in each sample (Figure 2.4b). After UV exposure, PTEO-GBP(3.8) exhibits a reduced glassy E'' and a smaller E'' peak. This is attributed to a high percentage of available GBP units

undergoing crosslinking reactions. At higher GBP loadings, the loss moduli of PTEO-GBP(12.6) and PTEO-GBP(16.3) remained virtually unchanged. These results suggest that all of the polymers underwent UV light initiated crosslinking, but PTEO-GBP(3.8) had the highest crosslinking efficiency. Figure 2.S9 displays further evidence suggesting that higher GBP loadings result in lower crosslinking efficiencies (i.e., percent conversion from GBP to crosslinks). In Figure 2.S9a, E' is plotted as a function of frequency. Here, it is evident that the storage modulus of PTEO-GBP(3.8) shows less frequency dependence than the storage modulus of PTEO-GBP(16.3). In general, elastic materials show less frequency dependent moduli than viscoelastic materials.⁵⁶ Therefore, PTEO-GBP(3.8) is more elastic than PTEO-GBP(16.3). The greater degree of elasticity in PTEO-GBP(3.8) is attributed to a higher percentage of its GBP units being consumed in crosslinking reactions. Higher crosslinking efficiency at lower crosslinker loading is attributed to higher reaction rates occurring at the surface of the samples, resulting in unreacted benzophenone groups in the interior of the samples. Copolymers with high GBP contents contained more benzophenone groups to begin with, so they retained more unreacted benzophenone on their interior than the sample with 3.8% GBP.

When PTEO-GBP with low GBP content is used as a binder, it produces composites with higher stiffness compared to PTEO-bound composites. The mechanical properties of the composites composed of sugar crystals and PTEO or PTEO-GBP were quantified using DMA. All of the sugar-polymer composites were composed of 90% sugar and 10% polymer by weight. Figure 2.5 displays the results of DMA experiments on sugar-polymer composites that did not receive a UV treatment. As can be seen in the E' , E'' , and $\tan \delta$ plots, the glass transition temperatures of the composites are larger than that of the pristine polymers by about 10 °C, as has been observed previously in other systems.^{57,58} The plot of E' vs. temperature reveals that increasing GBP content in PTEO as the binder increases stiffness up to 6 mol% GBP, in both the glassy and rubbery states (Figure 2.5a). The $\tan \delta$ curves of PTEO-GBP bound composites are also reduced compared to PTEO, indicating a smaller viscous response in the PTEO-GBP composites (Figure 2.5c). However, beyond 6% GBP, the stiffness decreases. This is evident by the drastically reduced E' of the composite using PTEO-GBP(12.6) as the binder (Figure 2.5a). Additionally, as seen in Figure 2.S10, when PTEO-GBP(8.5) is used as a binder, it has a reduced E' (Figure 2.S10a) and increased $\tan \delta$ (Figure 2.S10c) compared to the PTEO-GBP(6) bound composite.

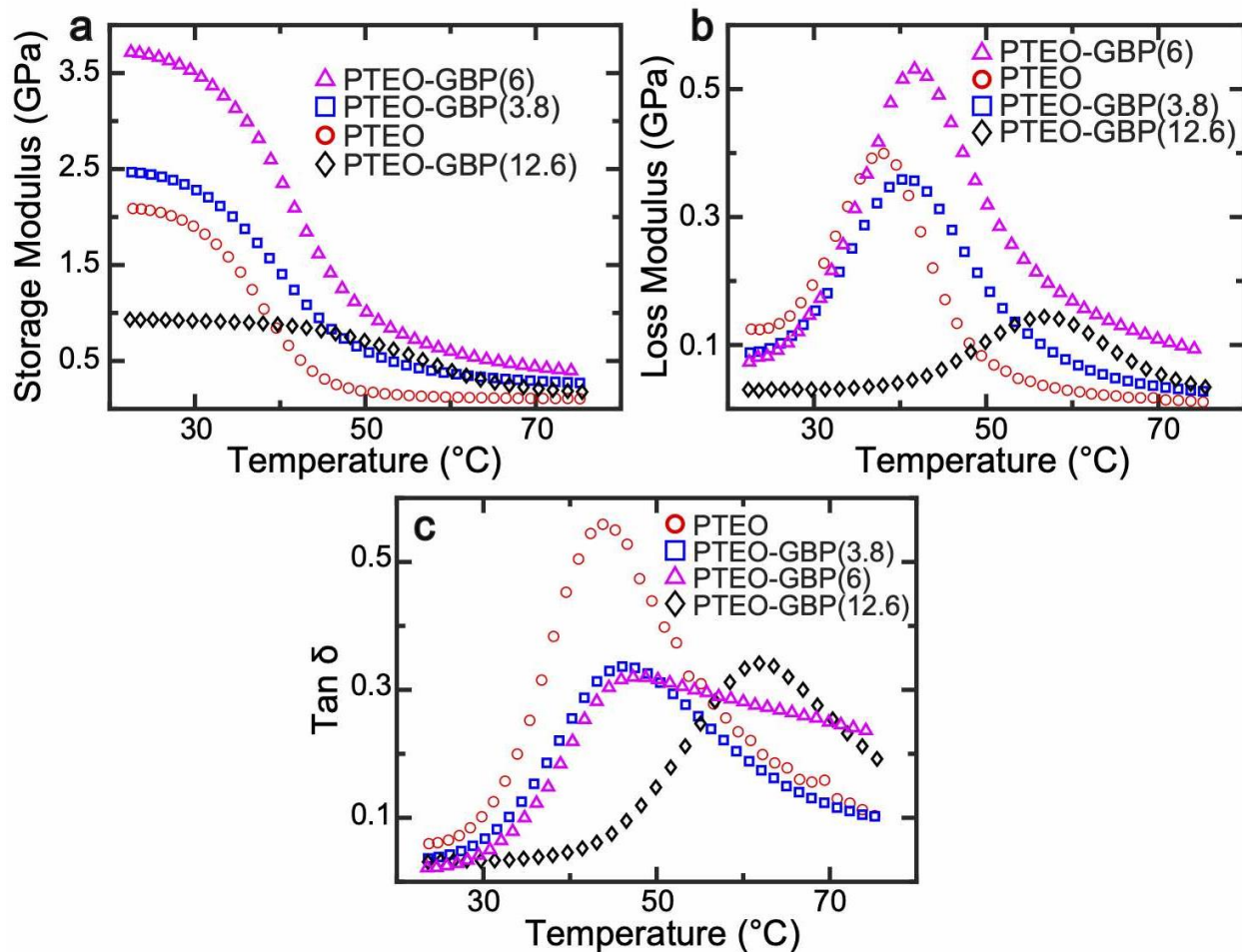


Figure 2.5. DMA results of 90% sugar-10% polymer composites (by weight) without UV treatment. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature. The legend indicates the percentage of GBP in the polymer, on a molar basis, used as the binder.

At low GBP percentages (i.e., $\leq 6\%$), the high solids content does not prevent thermal annealing from reversing the plasticizing effect of GBP. Alternatively, at higher GBP loadings and high sugar content, polymer chains are restricted from reorganizing due to the rigid crystals held in the polymer matrix. At higher GBP content, it is reasonable to envision that more extreme chain rearrangement is required to negate the plasticizing effect of GBP. When the sugar particles constrain chain rearrangement, the bulky GBP units remain in a configuration that space out polymer chains in highly loaded GBP polymers, resulting in a decreased E' . Additionally, the smaller E'' peaks in PTEO-GBP(12.6) and PTEO-GBP(8.5) composites suggest that they do not reorganize into a more rigid arrangement that releases a large amount of heat during chain slippage

(Figure 2.5b and 2.S10b). When used as a binder with high solids loading, PTEO with greater than 6% GBP appears to produce composites with reduced stiffnesses.

The viscoelastic behavior of PTEO and PTEO-GBP based composites resemble the viscoelastic behavior of PBX 9502. PBX 9502 consists of 95% 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) and 5% Kel F-800 polymer as the binder, on a mass basis.⁵⁹ TATB is one of the most insensitive high explosives used today, and Kel F-800 is a fluoropolymer with a T_g of $\sim 28^\circ\text{C}$.^{59,60} TATB can be made into a PBX with a glassy, high T_g polymer due to the supreme insensitivity of the explosive. Under similar experimental conditions, the storage modulus of PBX 9502 decreases from ~ 9 GPa at 20°C to ~ 3.5 GPa at 80°C . The damping factor increases from ~ 0.05 at 20°C to ~ 0.16 at 80°C .⁶¹ Therefore, the storage moduli of the composites bound by PTEO and PTEO-GBP are of the same order of magnitude of PBX 9502 and the damping factor across the measured temperatures are similar. In contrast to PBX 9502, PBX 9501 is composed primarily of 1,3,5,7-tetranitroazacyclooctane (HMX) bound with a softer, plasticized polymer, Estane ($T_g \sim -45^\circ\text{C}$).^{41,42} HMX is much more sensitive to shock than TATB,^{62,63} which requires the use of soft, rubbery binders that can dampen insults and decrease its shock sensitivity. PBX 9501 exhibits a storage modulus similar to PTEO and PTEO-GBP composites.⁴² However, the damping factor of PBX 9501 is noticeably higher than PTEO and PTEO-GBP based composites,⁴² especially below PTEO's T_g , demonstrating Estane's superior energy absorbing capability. Thus, PTEO and PTEO-GBP would be suitable to bind an insensitive high explosive like TATB but appear too stiff to bind a more sensitive explosive that requires a softer binder with a lower T_g and better damping ability.

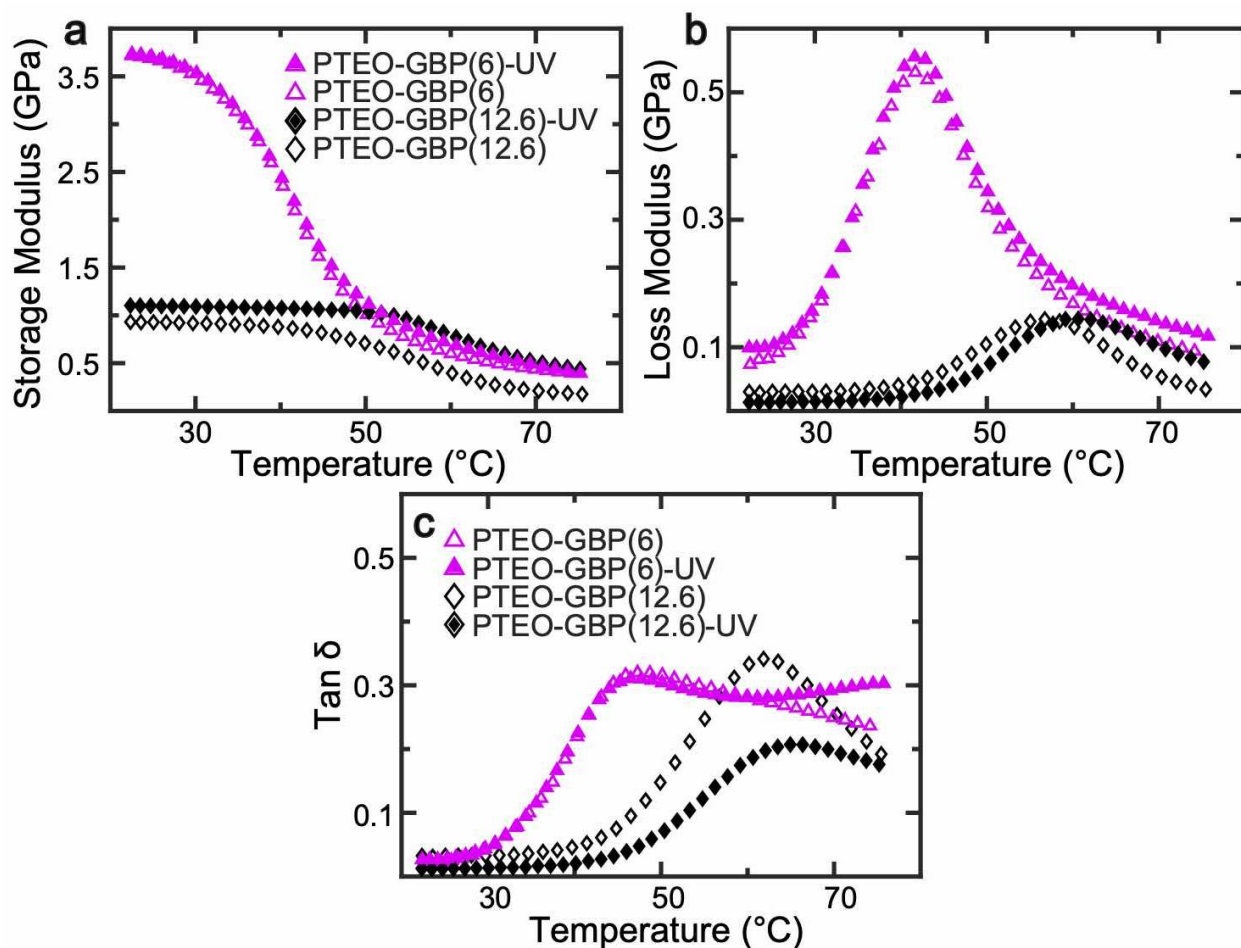


Figure 2.6. DMA results of 90% sugar-10% polymer composites before and after UV treatment. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature. Legend indicates the percentage of GBP, on a molar basis, in the polymer used as binder. Samples denoted as “-UV” received the UV treatment.

When PTEO-GBP bound composites were exposed to UV light, evidence of crosslinking was observed in a copolymer with relatively high GBP content in a similar manner to the pristine polymer samples. The E' , E'' , and $\tan \delta$ curves of PTEO-GBP(6) were virtually unchanged after the UV light treatment (Figure 2.6). In contrast, the PTEO-GBP(12.6) composite showed an increased E' , a decreased $\tan \delta$ peak, and an increased T_g after UV exposure (Figure 2.6). These data suggest that at high solids loading, a GBP loading of greater than 6% (on a molar basis) is required to elicit measurable UV crosslinking. In the neat polymer samples, GBP loadings as low as 3.8% initiated measurable crosslinking. Therefore, the high sugar content appeared to shield the PTEO-GBP(6) composite from receiving enough UV energy to allow for curing. Alternatively, at

12.6% GBP, there were enough benzophenone groups on the surface of the composite to generate a detectable change in mechanical properties. In the neat polymer, we observed a greater apparent conversion of GBP groups to crosslinks at lower GBP loadings. Nevertheless, there was evidence of crosslinking at high GBP loadings. In the case of sugar/polymer composites, measurable crosslinking only occurred at GBP loadings of >6 mol%. The PTEO-GBP(12.6) composite's $\tan \delta$ after UV crosslinking was significantly lower than the $\tan \delta$ of the PTEO-GBP(6) composite. However, in the rubbery region, the storage modulus of PTEO-GBP(12.6) (0.63 GPa) was only slightly higher than PTEO-GBP(6) (0.58 GPa), suggesting that only a small number of crosslinks were formed.

The addition of silver nanowires (AgNWs) imparted macroscopic electrical conductivity and mechanical reinforcement to the composites. Specifically, composites of PTEO, sugar, and (AgNWs) were fabricated. All of the the AgNW-containing composites contained 10% PTEO, 1-5% AgNWs, and 85-89% sugar, on a mass basis. When the AgNW content increased from 2 to 2.5 weight percent, the conductivity of the composites increased from $6.1 \times 10^{-4} \text{ S cm}^{-1}$ to 0.62 S cm^{-1} (Figure 2.7d). This large increase in conductivity signifies the formation of a network of AgNWs between the conductive PTEO domains.⁶⁴ The addition of AgNWs also affects the viscoelastic properties of the composite. While the storage modulus was only slightly increased, primarily in the rubbery region, after adding 0.5 and 2 wt% AgNWs to the composites (Figure 2.7a), there was a drastic increase in E' when AgNW content was increased from 2 to 3%.

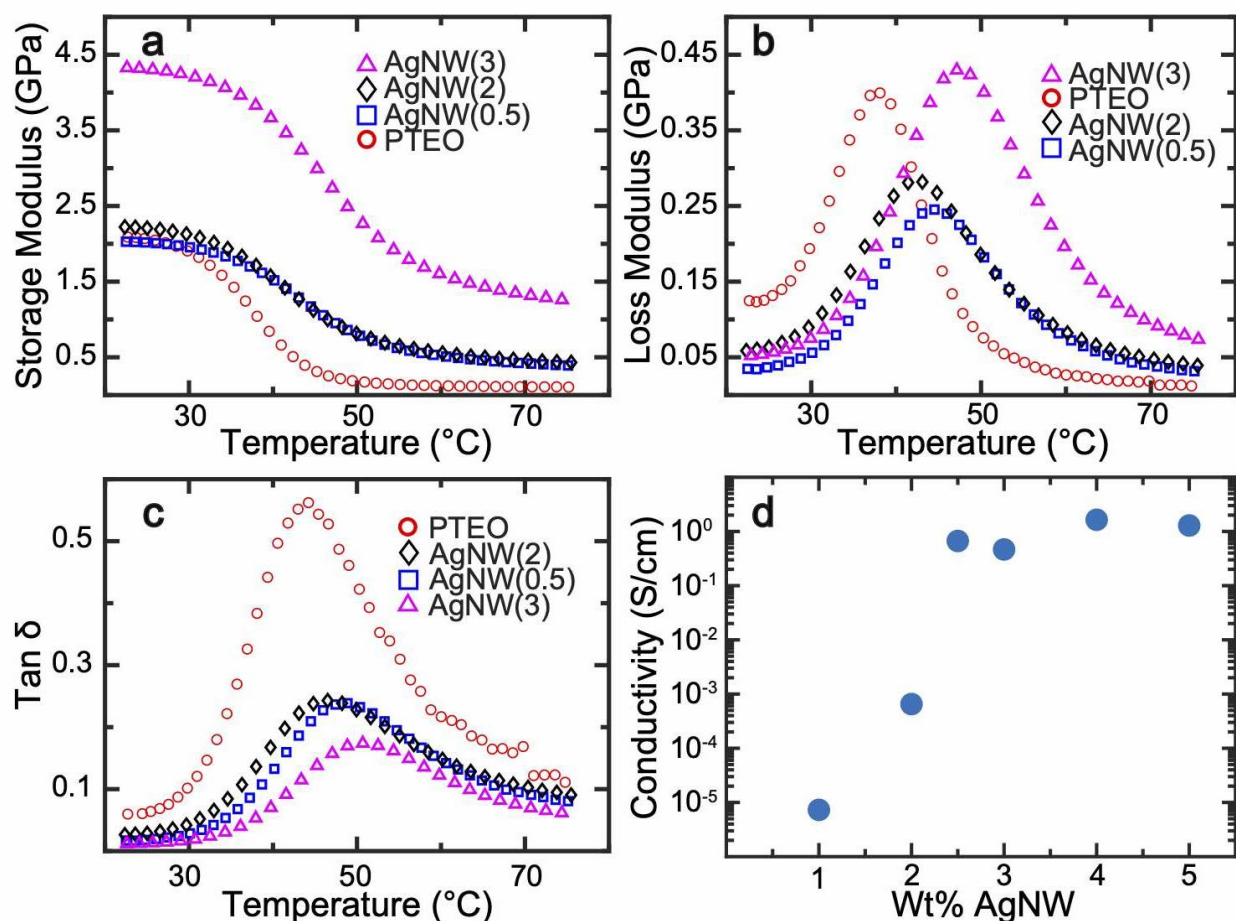


Figure 2.7. DMA and electrical conductivity results of sugar/PTEO/AgNW composites. All of the composites contained 90% solids content. For example, AgNW(3) is composed of 3% AgNWs, 87% sugar, 10% PTEO, on a mass basis. All of the PTEO used was PTEO homopolymer. Sample denoted as PTEO in the legend did not contain AgNWs. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ of composites versus temperature. (d) Conductivity of the composites as a function of nanowire loading.

The loss modulus decreased after adding 0.5 and 2% AgNWs (Figure 2.7b). Adding AgNWs decreased the damping of the composites, with 3% AgNWs having the smallest $\tan \delta$ across all temperatures (Figure 2.7c). The drastic stiffening of the composite observed between 2% and 3% AgNWs (on a mass basis) corresponds to the pathway formation around 2% as seen in the conductivity results. This is indicated by the precipitous rise in storage modulus and decrease in $\tan \delta$ from 2% to 3% AgNWs.

PTEO-GBP bound composites containing AgNWs had similar conductivity as PTEO-sugar-AgNW composites, but they had reduced elasticity. When the binders contained 1.8 and 5.0%

GBP, the composites had conductivities of the same order of magnitude as PTEO based composites (Figure 2.S11). However, the composites containing AgNWs bound by PTEO-GBP copolymers showed significantly reduced stiffnesses (Figure 2.S12). The storage modulus was reduced well below the PTEO-sugar-AgNW composites when PTEO-GBP was used as the binder (Figure 2.S12a). Their $\tan \delta$ peaks also increased significantly as compared to the PTEO-sugar-AgNW composites (Figure 2.S12c). Therefore, PTEO-GBP based composites containing AgNWs displayed reduced elasticity. An investigation into the interaction between PTEO-GBP and AgNWs could provide a pathway to overcoming this decreased stiffness.

2.4 Conclusions

A conducting radical polymer, PTEO, was used as the binder in a mock PBX. The radical polymer was copolymerized with a UV-active crosslinker (GBP) as a strategy to cure the polymer. Additionally, AgNWs were added to the mock PBX to confer macroscopic electrical conductivity to the composite. DMA analysis revealed that chain reorganization induced by thermal curing stiffened both the polymer and polymer/sugar composites when GBP was present. Evidence of UV-crosslinking of neat PTEO-GBP was observed at GBP loadings as low as 3.8%. In sugar-polymer composites, crosslinking was only observed when the binder contained higher loadings (i.e., ~10% GBP). Therefore, we propose molecular design strategies to adjust the mechanical properties of PBXs using a radical polymer-based binder with thermal and UV curing methods. We also suggest a combined radical polymer-nanocomposite strategy to confer electrical conductivity to composites that could provide utility in the development of highly electrically conductive energetic composites.

2.5 Supplementary Information

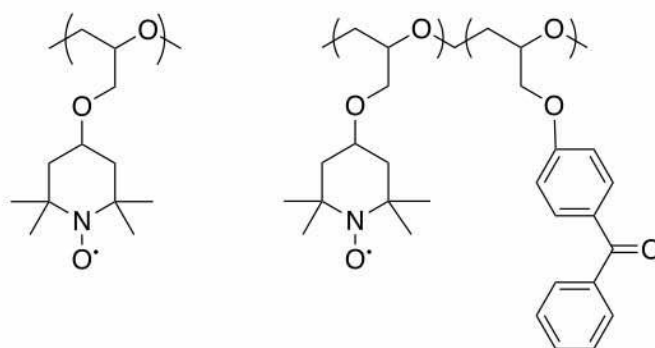


Figure 2.S1. Chemical structures of polymers used as binders. Left: PTEO. Right: PTEO-GBP.

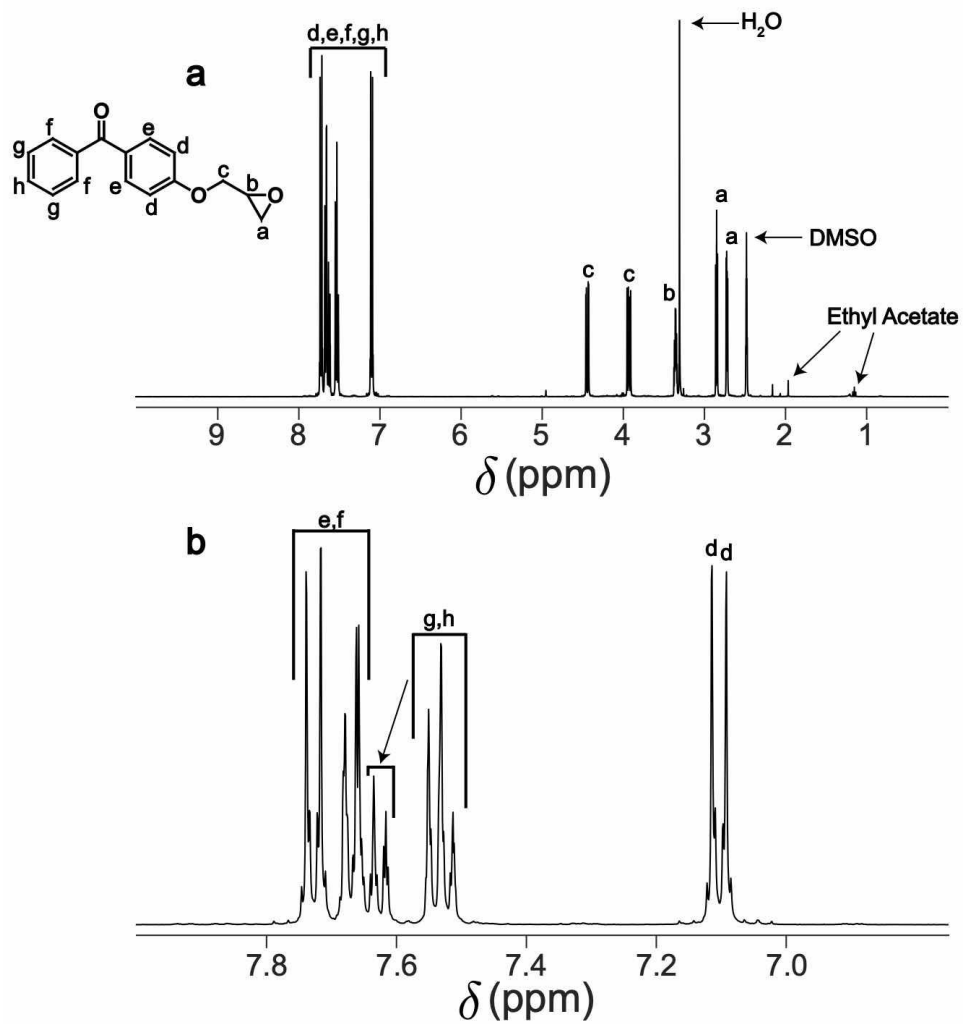


Figure 2.S2. NMR Characterization of GBP. (a) Full spectrum. (b) Aromatic region of the spectrum.

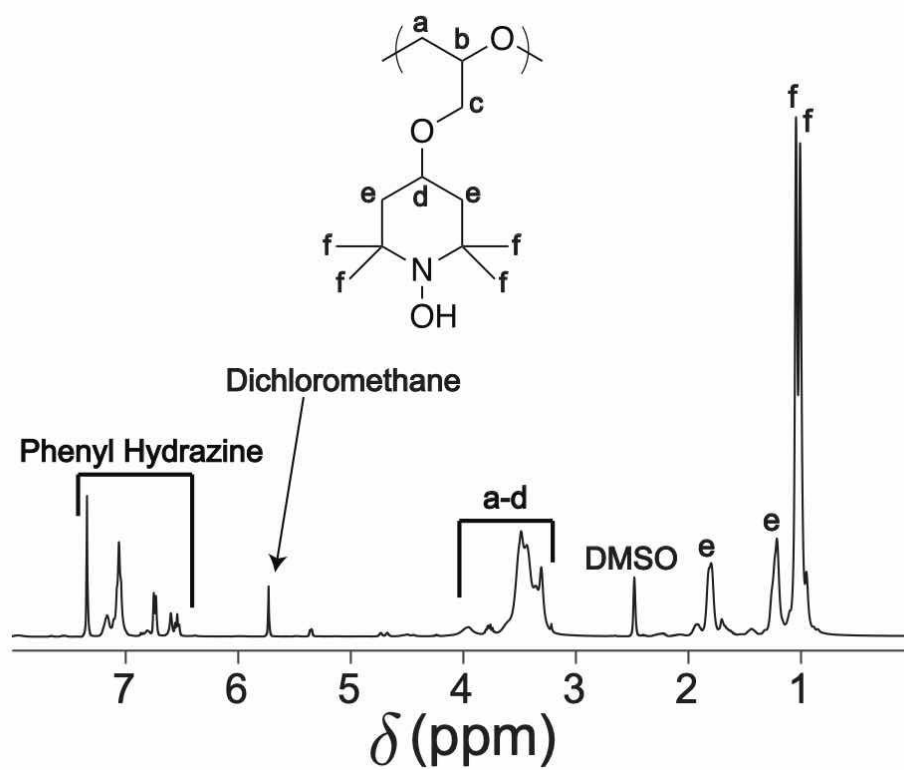


Figure 2.S3. NMR Characterization of PTEO.

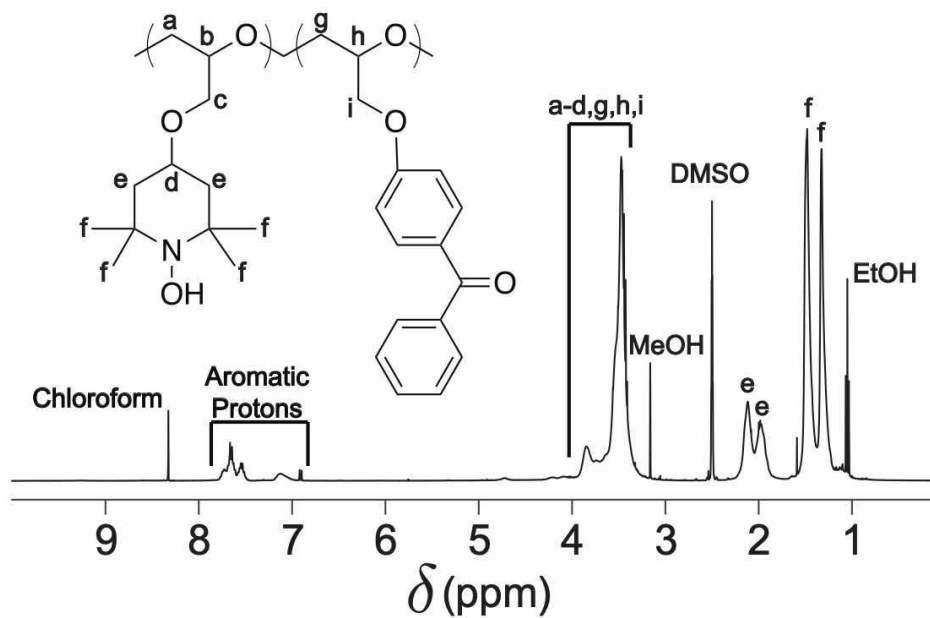


Figure 2.S4. NMR Characterization of PTEO-GBP.

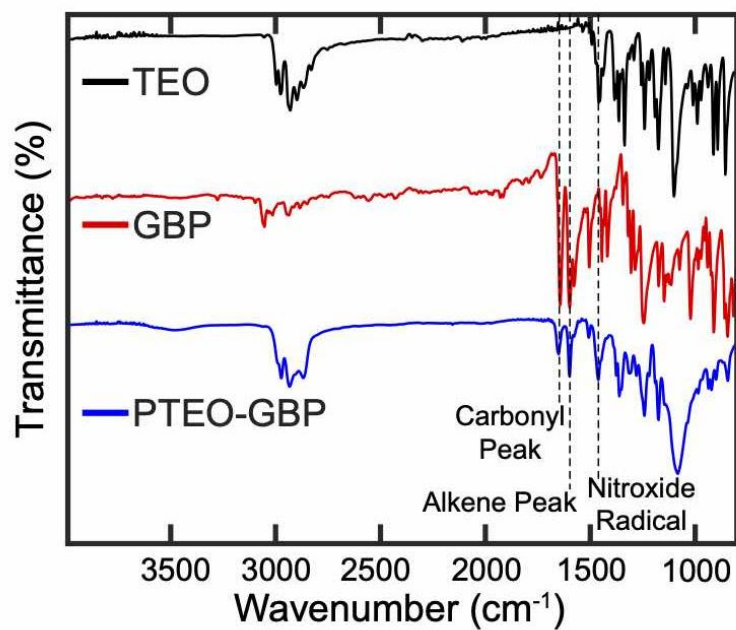


Figure 2.S5. FTIR characterization of TEO, GBP, and PTEO-GBP.

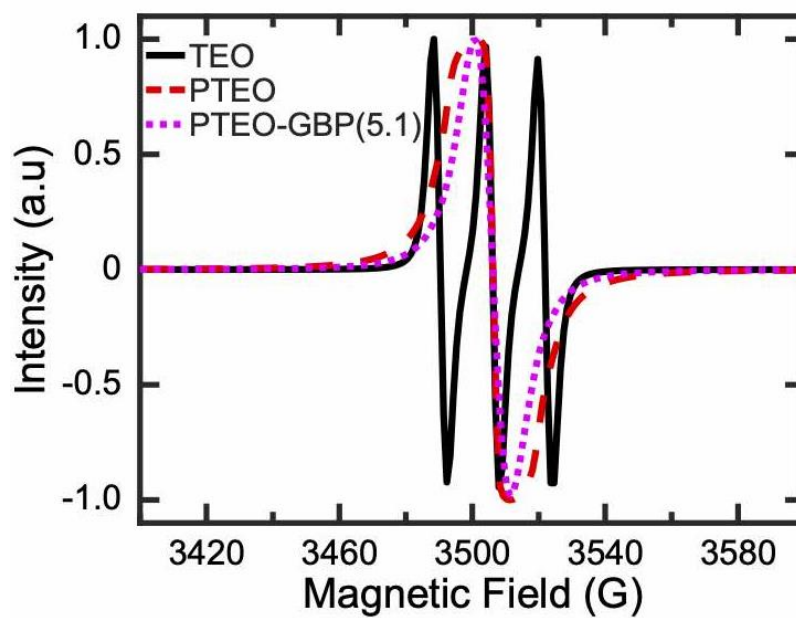


Figure 2.S6. EPR Characterization of PTEO and PTEO-GBP.

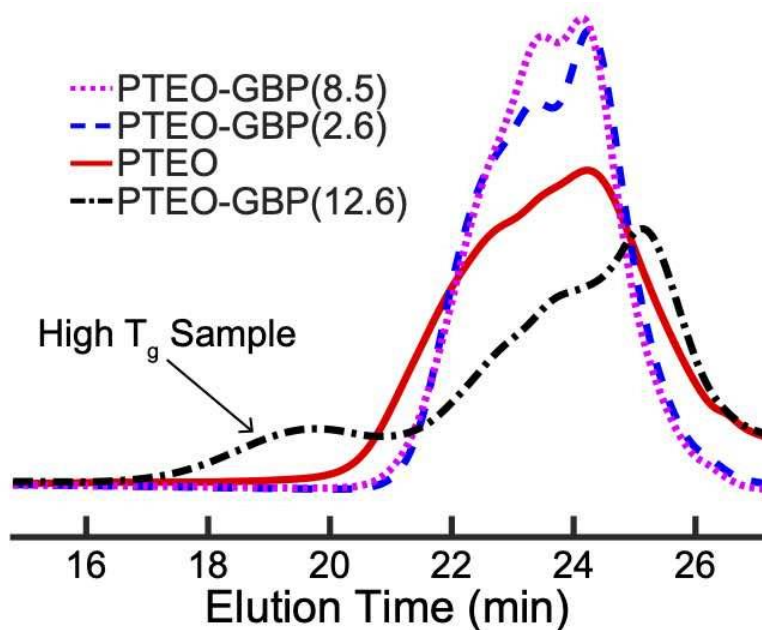


Figure 2.S7. SEC traces of PTEO and PTEO-GBP polymers. The synthetic procedure produced consistent molecular weights. PTEO-GBP(12.6) had an anomalous molecular weight distribution, resulting in a significantly higher glass transition temperature as determined by DMA. Number average molecular weight (M_n) of PTEO = 4720 g/mol, Polydispersity (PDI) of PTEO = 2.25. PTEO-GBP(2.6) M_n = 5150 g/mol, PDI = 1.88. PTEO-GBP(8.5) M_n = 5073, PDI = 1.77. PTEO-GBP(12.6) first peak M_n = 152354 g/mol, PDI = 2.72. PTEO-GBP(12.6) second peak M_n = 2316 g/mol, PDI = 3.30.

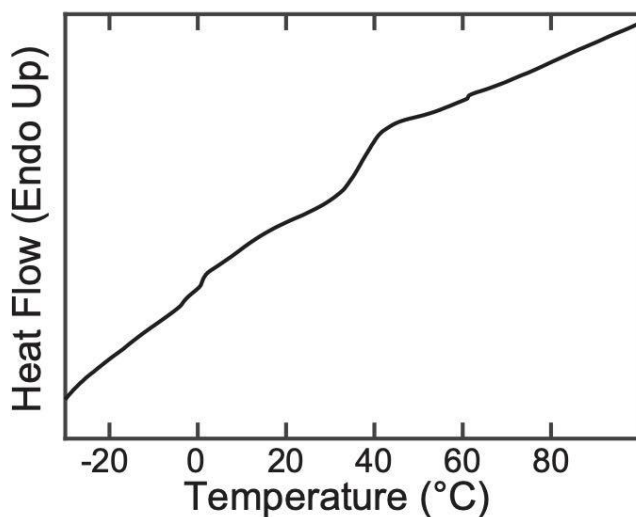


Figure 2.S8. DSC thermograph of PTEO-GBP(19.4) exhibiting two apparent glass transitions at ~0 °C and ~40 °C.

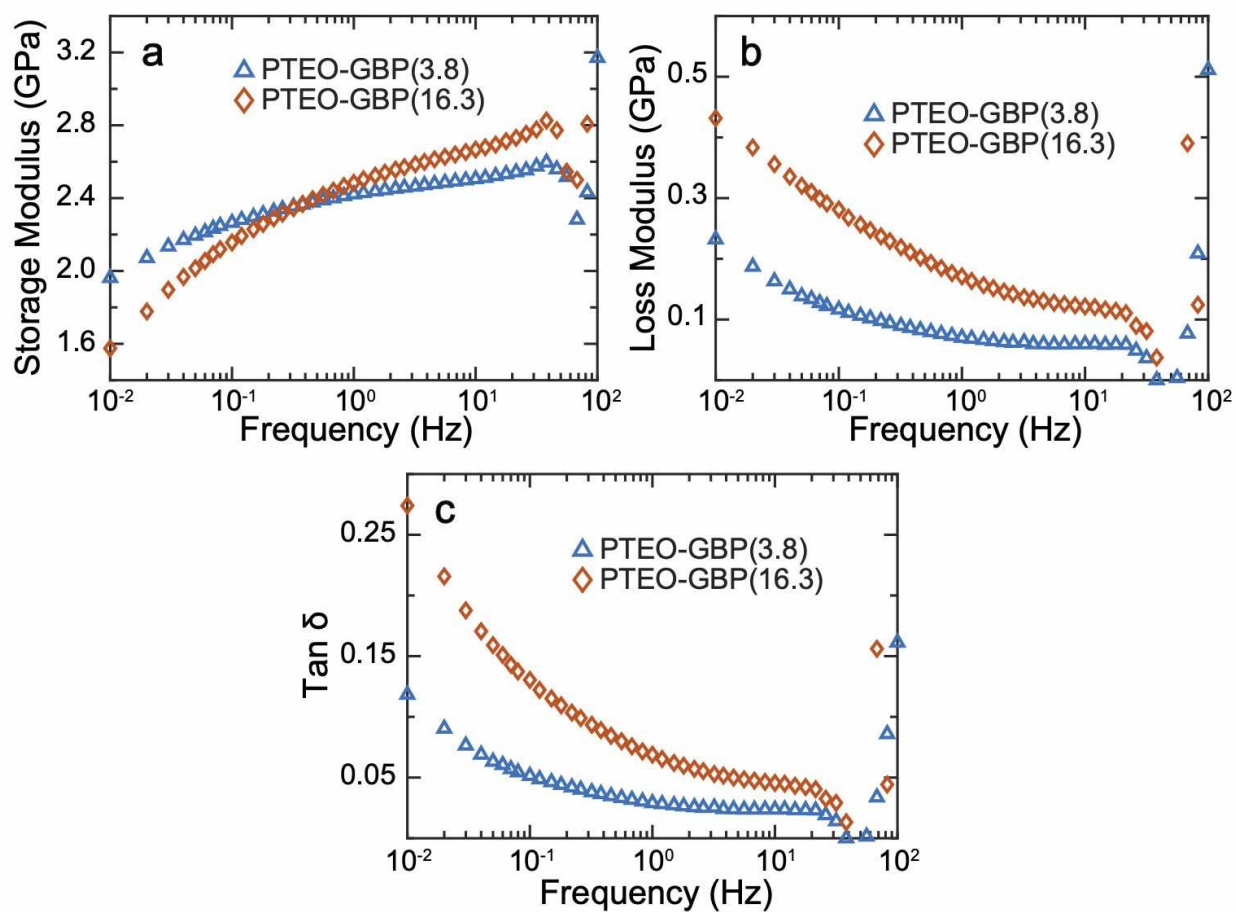


Figure 2.S9. Frequency sweep DMA experiments of neat PTEO-GBP(3.8) and PTEO-GBP(16.3) samples after UV crosslinking. (a) Storage modulus, (b) loss modulus, and (c) tan δ is plotted from 10^{-2} to 10^2 Hz.

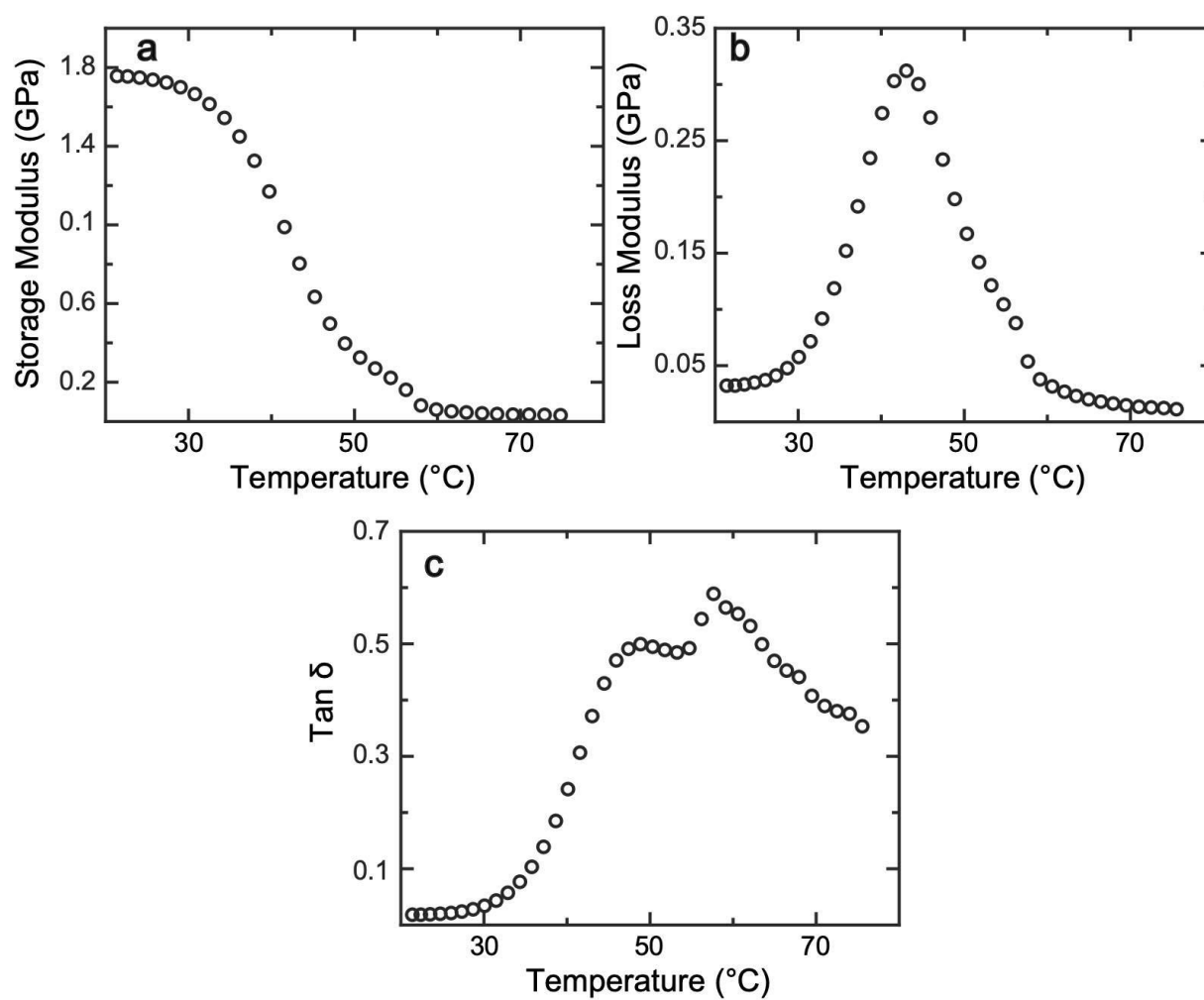


Figure 2.S10. DMA of a composite composed of 90 wt% sugar and 10 wt% PTEO-GBP(8.5) as the binder. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ plotted versus temperature.

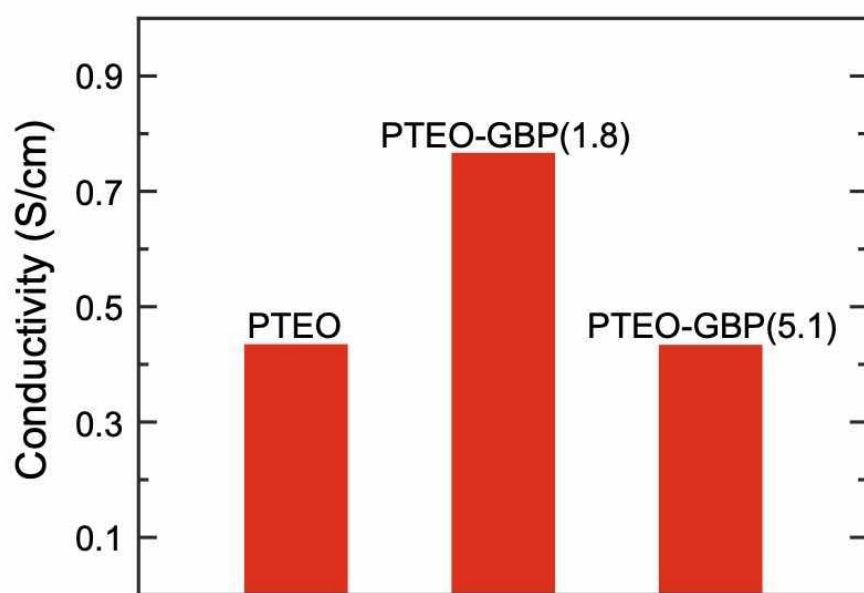


Figure 2.S11. Conductivity of composites composed of 87 wt% sugar, 10 wt% binder, and 3 wt% AgNWs. Conductivities of the composites are displayed when PTEO, PTEO-GBP(1.8), and PTEO-GBP(5.1) was used as the binder.

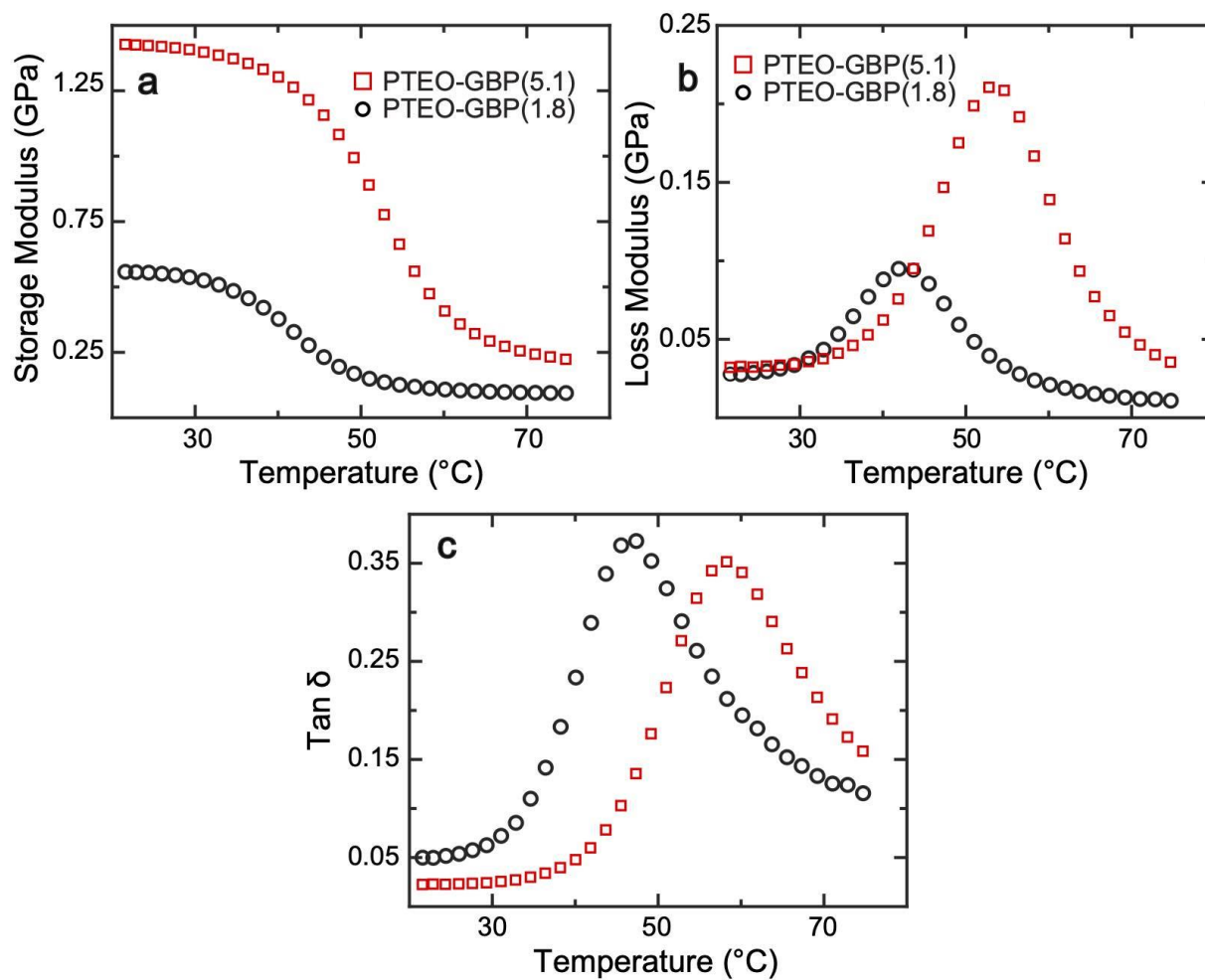


Figure 2.S12. DMA of composites composed of 87 wt% sugar, 10 wt% PTEO-GBP binders, and 3 wt% AgNWs. The binders used were PTEO-GBP(1.8) and PTEO-GBP(5.1). (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ are plotted versus temperature.

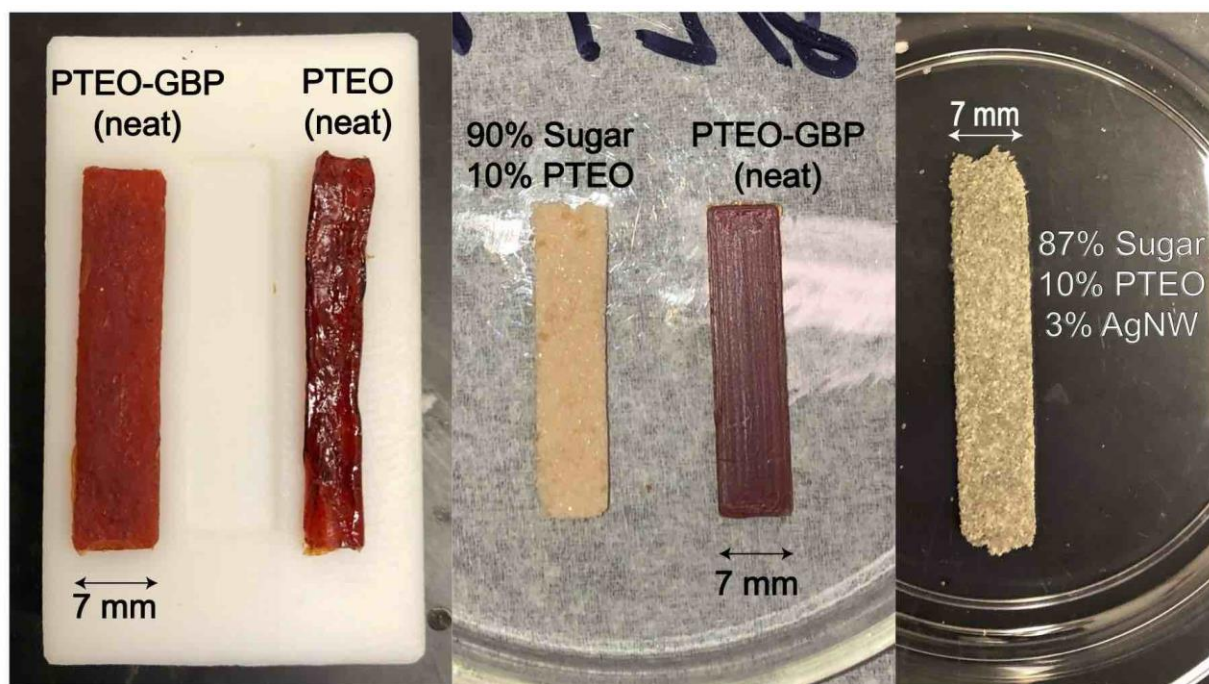


Figure 2.S13. Pictures of DMA samples. *Left Image:* Neat PTEO-GBP sample (left) and neat PTEO homopolymer sample (right). *Middle Image:* 90% Sugar/10% PTEO sample (left) and neat PTEO-GBP sample (right). *Right Image:* 87% sugar/10% PTEO/3% AgNW sample. All of the samples are ~30mm x 7mm x 1mm besides the PTEO homopolymer sample.

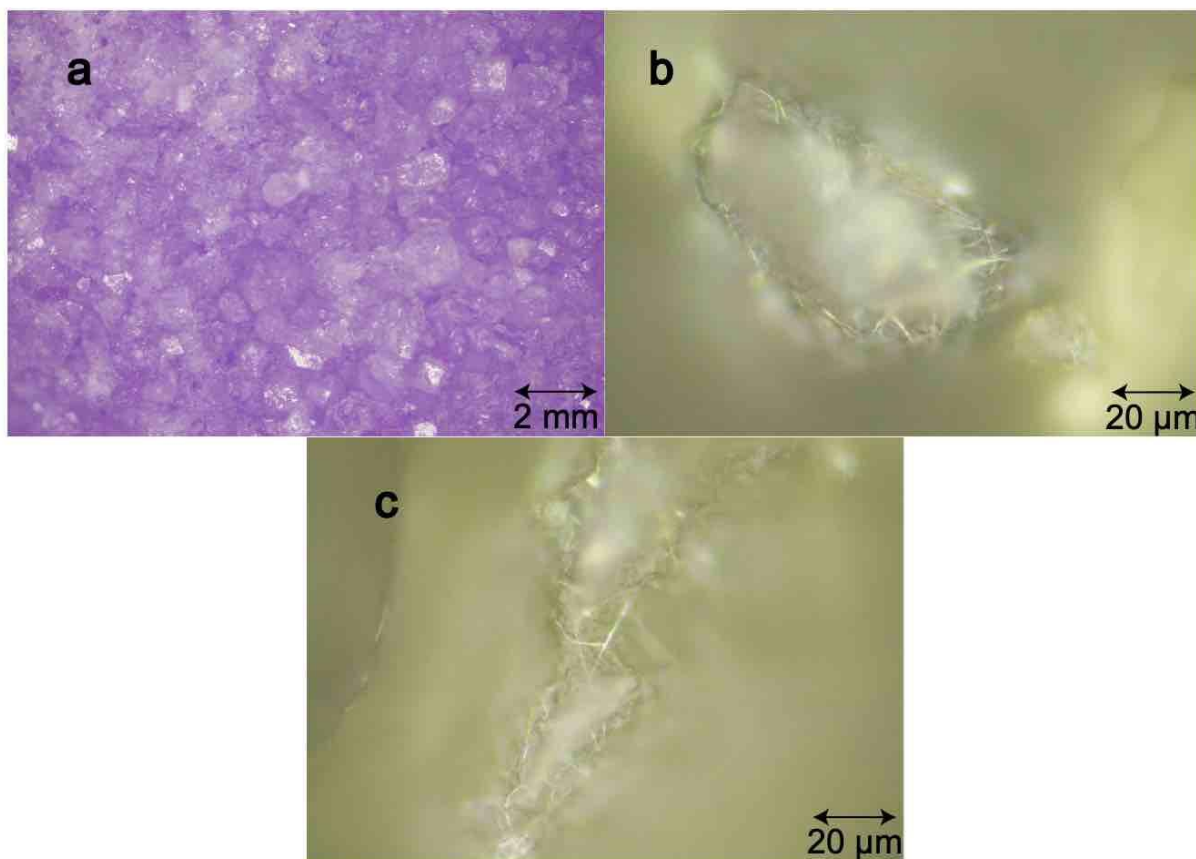


Figure 2.S14. Optical microscopy images of 87% sugar/10% PTEO/3% AgNW sample. (a) Sugar crystals visible in PTEO matrix. (b),(c) AgNWs visible on the surface of sugar crystals.

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3. CONCLUSIONS AND FUTURE WORK

3.1 Conclusions

In Chapter 2, a mock energetic material with high solids loading and electrical conductivity was reported. Conductive radical polymers, poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) and PTEO-*co*-glycidyloxybenzophenone (PTEO-GBP), were used as binders and sugar particles, the inert solid filler, were loaded at 90% (by weight). Silver nanowires (AgNWs) were added at loadings ranging from 0% to 5% and macroscopic conductivities of $\sim 1 \text{ S cm}^{-1}$ were observed. The viscoelastic behavior of the polymers and the composite materials were characterized by dynamic mechanical analysis (DMA). The viscoelastic behavior of PTEO and PTEO-GBP-bound composites was similar to Kel F-800-bound plastic bonded explosives (PBXs). Specifically, PTEO and PTEO-GBP exhibited a similar glass transition temperature (T_g) to that of Kel F-800 ($\sim 30^\circ \text{C}$), similar storage moduli, and similar damping factors across the measured temperatures.¹ Thus, PTEO and PTEO-GBP could bind an insensitive explosive, such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), that does not require a soft, desensitizing binder with a low T_g . This effort represents the first step in developing a highly conductive energetic composite with the ability to be resistively heated. Further experimentation and optimization of the system will determine the utility and performance of the proposed composite.

3.2 Future Work

The DMA results of the neat polymers and the sugar composites give a sense of the mechanical behavior of these materials over a wide range of temperatures. However, compressive and tensile stress-strain experiments are needed to determine the moduli, the strength, and the strain capability of the polymers and composites. Because stress-strain tests are frequently performed on energetic materials, these experiments will provide more data by which to compare the proposed energetic composite to commonly used energetic materials.²⁻⁹ Additionally, these experiments will further elucidate the effect the crosslinker (GBP) and AgNWs have on the mechanical properties of the composites. Furthermore, the composites discussed in Chapter 2 contained a monomodal size distribution of sugar particles with a mean particle diameter of $150 \mu\text{m}$. Using a bimodal particle size distribution could enhance the solids loading capability of PTEO

and PTEO-GBP by improved packing of the particles in the polymer matrix. Thus, manipulating the particle size distribution of the composite material could provide a method to improve the mechanical properties.

The composites discussed in Chapter 2 were prepared by a solvent-antisolvent method due to the relatively high T_g of PTEO and PTEO-GBP and its high viscosity above its T_g . Lowering the T_g of the polymer and decreasing its viscosity could allow PTEO-based and PTEO-GBP-based composites to be processed by a cast-curing procedure. This could be accomplished by adjusting the PTEO to GBP ratio in the copolymer, adding a plasticizing agent, or a combination of the two strategies. The ability to prepare PTEO-based composites by solvent-antisolvent and cast-curing methods would provide more flexibility in the processing of such composites and thus, expand the potential applications of the material.

The motivation in designing an electrically conductive energetic material is to give the material the ability to be heated upon the application of an electric current (i.e., resistive heating). Thus, experiments that quantify the resistive heating ability of the composite material are needed. Preliminary tests of the kind have been performed but heating of the material was primarily observed at the interface between the electrical contacts and the mock energetic material. This effect is attributed to poor contact between the electrode and the composite, which resulted in charge accumulation and hot spot formation. Therefore, annealing the composite material above the T_g of the binder with electrical clips attached could result in improved contact of the electrodes and eliminate hot spot formation at the contacts. Then, the resistive heating ability of the composite can be observed without the interfacial effects present in previous experiments. With an understanding of the resistive heating ability of the mock energetic material, the usefulness of the material in modern applications will be better established.

PTEO and PTEO-GBP were chosen as the binders in the conductive composite due to their proven ability to conduct electrons at length scales < 600 nm.^{10,11} AgNWs were added to connect electrically conductive domains of PTEO, thus allowing the material to conduct at the macroscale. The contribution of the radical polymer to the macroscopic conductivity of the composite could be investigated by fabricating a composite material containing AgNWs that is bound by an electrically insulating polymer. The conductivity of such a composite would shed light on the degree to which the radical network provided by PTEO contributes to the macroscopic electrical conductivity.

After preliminary mechanical, electrical, and thermoelectric properties of the mock energetic material have been measured, its compatibility with live energetics must be ensured. After mixing PTEO and PTEO-GBP with live energetics, differential scanning calorimetry (DSC), impact, friction, and electrostatic discharge sensitivity tests can be performed to ensure the sensitivity and safety profile of the energetic composites are acceptable. Then, the mechanical and electrical characterization of the energetic composite can be performed and compared to the mock energetic material.

The electrically conductive energetic composite proposed here shows promising conductivity and high solids loading capability. This suggests that the material possesses the ability to be resistively heated, which could provide utility in energetics applications. The viscoelastic response of the material as determined by DMA reveals relatively stiff behavior, relative to other energetic composites. Decreasing the stiffness and viscosity of the polymer binders presented here could broaden the scope of their potential application in energetic materials. Lastly, further mechanical and electrical characterization is necessary to determine the ultimate utility of the material in modern energetic applications.

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