Polyamine–Diazirine Conjugates for Use as Primers in UHMWPE–Epoxy Composite Materials

R. Nazir, L. Bi, S. F. Musolino, O. H. Margoto, K. Çelebi, C. Mobuchon, M. Takaffoli, A. S. Milani, G. Falck, & J. E. Wulff

2022

R. Nazir, L. Bi, S. F. Musolino, O. H. Margoto, K. Çelebi, C. Mobuchon, M. Takaffoli, A. S. Milani, G. Falck, and J. E. Wulff (**2022**) Polyamine–Diazirine Conjugates for Use as Primers in UHMWPE–Epoxy Composite Materials. *ACS Applied Polymer Materials*, *4*, 1728–1742. *(link)*

Polyamine–Diazirine Conjugates For Use As Primers In UHMWPE–Epoxy Composite Materials

*Rashid Nazir[a], Liting Bi[a], Stefania F. Musolino[a], Olivia H. Margoto[b], Kuthan Çelebi[c], Christophe Mobuchon[c], Mahdi Takaffoli[d], Abbas S. Milani[b,d], Greg Falck[e], Jeremy E. Wulff[a,f]**

[a] Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6, Canada.

[b] Composites Research Network (CRN), University of British Columbia, Kelowna, BC, V1V 1V7, Canada.

[c] Composites Research Network (CRN), University of British Columbia, Vancouver, BC, V6T 1Z4, Canada.

[d] Materials and Manufacturing Research Institute (MMRI), University of British Columbia, Kelowna, BC, V1V 1V7, Canada.

[e] Aluula Composites, Victoria, BC, V8Z 1T3, Canada.

[f] Centre for Advanced Materials and Related Technology (CAMTEC), University of Victoria, Victoria, BC, V8P 5C2, Canada.

*E-mail: wulff@uvic.ca.

KEYWORDS: polymer composites, UHMWPE, diazirines, crosslinking, primers.

ABSTRACT: Ultra-high molecular weight polyethylene (UHMWPE) fibers show promise for use in fiber reinforced polymer composites, but have poor interfacial adhesion to the epoxy resin that would serve as the polymer matrix. Here we describe the development of a diazirine-grafted polyamine that can be used as a topically applied primer for UHMWPE fibers. Activation of the diazirine groups on the primer initiates C–H bond insertion on the polyethylene fiber, leading to strong covalent bonds between the fiber and the polyamine coating. The covalently functionalized surface can then engage in nucleophilic addition reactions with epoxy resin—resulting in increased bonding to the epoxy matrix (demonstrated through lap-shear experiments) and increased performance for fiber reinforced composite materials (demonstrated through lamination rates and short-beam stress measurements).

INTRODUCTION

The aerospace and automotive industries increasingly rely upon light-weight, high-strength fiber reinforced polymer composites for manufacturing.[1,2] The polymer matrix for these composite materials is frequently some form of epoxy resin, while the fiber reinforcing agent is either fiberglass or carbon fiber.[3] However, while fiberglass–epoxy and carbon fiber–epoxy composites have many desirable properties that have encouraged their widespread use (e.g. high stiffness and excellent compressive strength) there remain important limitations. For example, both glass and carbon fibers suffer from unwanted brittleness,[4] and both types of strengthening fibers have an undesirably high density (*ca.* 2.5 g/cm^3 for E-glass or S-glass; 1.75–2.00 g/cm^3 for carbon fiber).[5] There is therefore considerable interest in developing epoxy composites that can make use of alternative fiber reinforcing agents.[6]

Ultra-high molecular weight polyethylene (UHMWPE) fiber is a good candidate as a fiber reinforcing agent, since its high ultimate tensile strength (≥ 2.9 GPa) and low density (0.97 g/cm^3) combine to give a high specific strength (Table S1).[7,8] Unfortunately, there is a mismatch between the very lipophilic (i.e. low surface energy; *ca.* 28–35 mJ/m^2) UHMWPE fiber and the polar (i.e. high surface energy) epoxy matrix. As a result, it remains difficult to prepare good-quality UHMWPE–epoxy composites without relying on destructive and expensive surface treatments (e.g. corona discharge, plasma treatment, or exposure to harsh chemical oxidants) that are used to oxidize the polyethylene surface and make it more receptive to binding with the epoxy matrix.[9] While such methods do afford increased adhesion between the polyethylene fiber and the matrix,[10] they can result in chain-fragmentation and other undesirable processes that compromise the integrity of the fiber.

We and others have shown that diazirine-based reagents can be useful for crosslinking and/or functionalizing low-functionality commodity polymers, including polyethylene (Figure 1A).[11,12,13,14,15,16] The diazirine group can be activated thermally (by treatment with temperatures above 100 °C) or photochemically (by excitation with 350–365 nm light),[17,18] or else through the application of an electric potential (–1.6 V vs. Ag/AgCl)[19] or through the use of a photosensitizer.[20,21] In all cases, high-energy carbenes are produced, which engage in promiscuous C–H insertion reactions along the aliphatic backbone of the polymer. This process, which results in the installation of strong covalent linkages to the polymer surface, can be harnessed to irreversibly link dyes[15] and photosensitizers[11(c)] to polymers, and can also be exploited in fabric strengthening[11(a)] and adhesion applications.[11(b)]

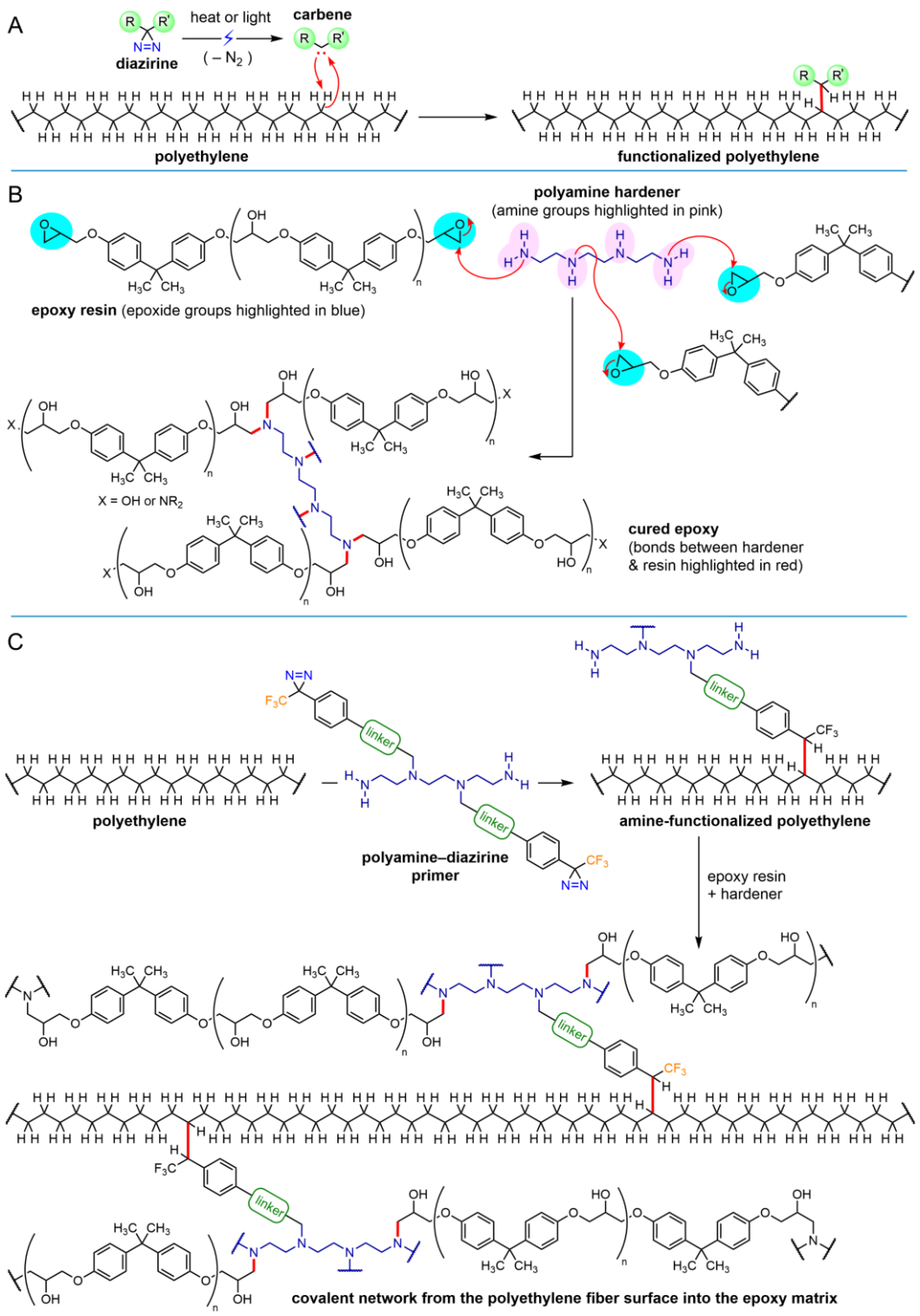


Figure 1. Development of a covalent primer to enhance the interaction of UHMWPE and epoxy. A: Functionalization of polyethylene using diazirines. B: Chemistry underpinning two-component epoxy systems. C: Proposed use of polyamine–diazirine conjugates to covalently functionalize

polyethylene fibers, allowing for the formation of polyethylene–epoxy composite materials. Critical new bonds are indicated in red. The value of n varies widely among different epoxy formulations, with values as low as 1 being possible.

Building upon these results, we hypothesized that a diazirine–polyamine conjugate could be used to covalently functionalize a polyethylene surface with amine groups, which in turn could participate directly in nucleophilic addition reactions with epoxy resin (Figure 1B-C). The result would be a strong adhesive force between the (now-functionalized) surface of the polyethylene fiber and the epoxy matrix. To explore this hypothesis, we prepared three types of diazirine–amine conjugates, varying the size of the amine component from a small molecule (triethylenetetramine; TETA) to a dendrimer (5^{th} generation poly(amidoamine); PAMAM-G5) and finally to a branched polymer (800 and 25,000 g/mol polyethylenimine; PEI). Here we show that the larger PEI–diazirine conjugate afforded excellent irreversible bonding to woven UHMWPE cloth, and facilitated its reaction with epoxy resin. Likewise, lap-shear samples prepared from UHMWPE bars treated with PEI–diazirine conjugate and then subsequently bonded together using a commercial epoxy/hardener mixture showed adhesion comparable to those of higher surface energy materials—consistent with the formation of a covalent network extending from the polyethylene surface into the epoxy matrix. Finally, we show that epoxy composites constructed from UHMWPE fabric that had been pre-treated with PEI–diazirine showed significantly improved uptake of epoxy during the resin impregnation step (relative to untreated controls), and had significantly improved mechanical properties when challenged in subsequent three-point bending experiments. Together, these data suggest a role for diazirine-enabled polyamines as epoxy primers for use with unfunctionalized polyolefins.

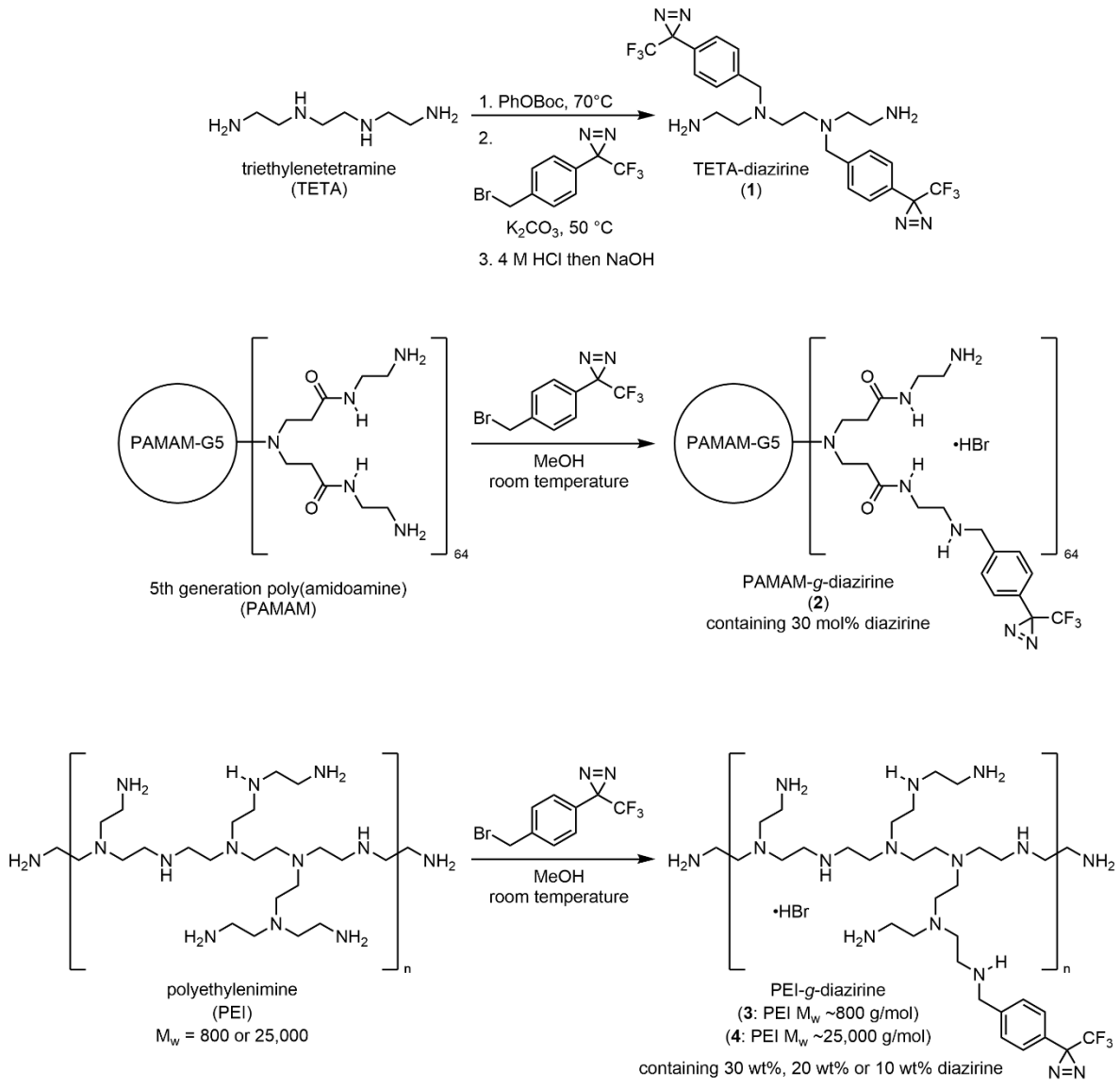
RESULTS AND DISCUSSION

1. Primer Design and Synthesis

Commercial two-component epoxy/hardener systems often consist of a linear telechelic polymer that terminates in epoxide groups (i.e. 'epoxy resin') and a hardener that incorporates multiple nucleophilic groups—usually amines or thiols. When mixed together, the nucleophilic residues within the hardener can add to the electrophilic epoxide groups in the epoxy resin. This results in the formation of multiple crosslinks throughout the material (Figure 1B), transforming the liquid resin (a thermoplastic) into a hard, non-meltable solid (a thermoset). Surface-bound amines can also react with epoxy resin, and this strategy has been leveraged by other groups to achieve enhanced bonding within carbon fabric-, graphene oxide- and silica-epoxy composites.[22,23,24]

UHMWPE nominally contains only C–C and C–H bonds, and so does not readily lend itself to the installation of amine groups using traditional function group manipulation strategies. In order to imbue UHMWPE fiber with surface amines (as illustrated in Figure 1C), we constructed three different diazirine–amine conjugates of varying size (Scheme 1). The smallest of these, TETA-diazirine (**1**), was designed based upon the triethylenetetramine reagent (TETA) that is found in commercial epoxy hardener cocktails. The internal amine groups of TETA were functionalized with diazirine groups, leaving the terminal amines free for reaction with the epoxy resin. For a diazirine–amine conjugate of intermediate size, we turned to the PAMAM–diazirine conjugate (**2**) popularized by the Steele group for use in wound healing.[19] Thus, 5th-generation poly(amidoamine), containing 128 surface amine groups, was reacted with 30 mol% of 3-[4-(bromomethyl)phenyl]-3-(trifluoromethyl)-3*H*-diazirine. Finally, polymeric diazirine–amine conjugates **3** and **4** were prepared by reacting branched polyethylenimine (800 g/mol or 25,000 g/mol) with either 30, 20, or 10 wt% 3-[4-(bromomethyl)phenyl]-3-(trifluoromethyl)-3*H*-

diazirine.[25] NMR analysis indicated that each diazirine–amine conjugate contained the expected ratio of labeled to unlabeled amine groups (see Table S2 in the Supporting Information).



Scheme 1. Synthesis of diazirine–amine conjugates. Structures for conjugates **2**, **3** and **4** are meant to convey approximate statistical relationships between free amine groups and diazirine labels, and are not intended to indicate the precise locations of the diazirine group within the polymer.

2. Reaction of Primers with UHMWPE Fabric and Reaction of Primer-Treated Fabric with Epoxy Resin

To explore which of polyamine–diazirine conjugates **1**–**4** provided the best immobilization to UHMWPE fibers following thermal activation, each compound was dissolved in methanol, and added to 75 g/m^2 woven UHMWPE fabric (200 denier) at a targeted loading of 10, 5, and 1 weight percent, relative to the mass of fabric. Because we know from previous work[11(a)] that *ca.* 25% of added diazirine reagent is typically lost to the aluminum incubation pan (this can be recovered and reused following the incubation step), the added mass of primer in each case was increased accordingly, to 12.5 wt%, 6.5 wt%, and 1.25 wt%. A vehicle control sample was also prepared, which was treated identically to the other samples, but with 0 wt% added primer). Additional control samples were prepared using 800 and 25,000 g/mol PEI with no diazirine grafting.

The fabric was incubated in the methanolic primer solutions for 30 minutes, after which the solvent was allowed to evaporate from the fabric. The resulting samples of primer-impregnated woven UHMWPE were then incubated at 110 °C for 4 hours to activate the diazirine groups.

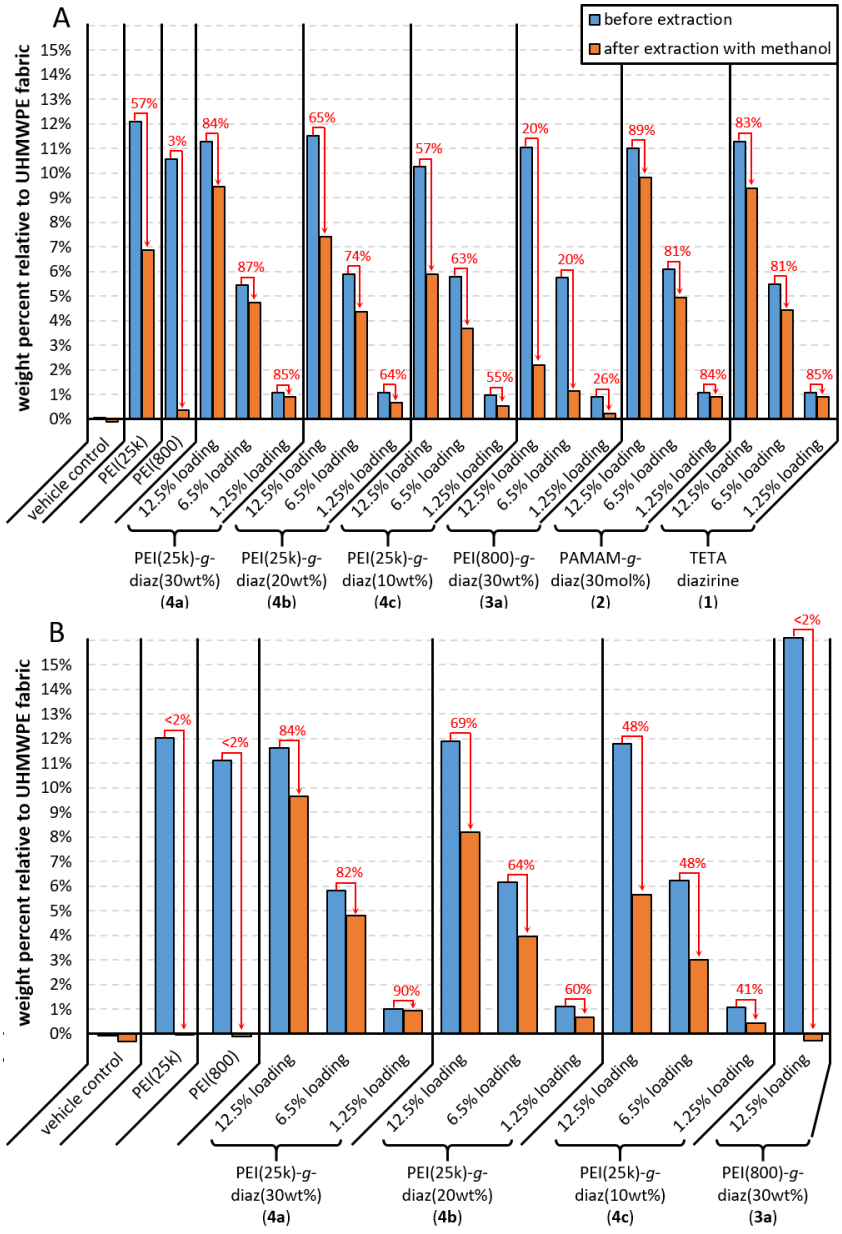


Figure 2. Effect of thermal activation (panel A) and photochemical activation (panel B) on primer loading. Numbers in red indicate the percent of primer retained following methanol extraction.

After activation, the samples were each weighed to determine the total amount of impregnated primer, and then were extracted three times with methanol to remove any reaction products that

were not covalently linked to the fabric. After drying the primer-treated fabrics, each sample was weighed again to determine the mass of primer that remained attached to the UHMWPE fiber.

The data (Figure 2A) indicated that the soaking procedure was successful in impregnating approximately the desired amounts of polyamine into each fabric sample (i.e., *ca.* 10%, 5% or 1%; refer to the blue bars in Figure 2A). Following extraction with methanol, an average of 85% of the primer was retained in the PEI(25k)-*g*-diazirine(30wt%) samples (**4a**) and the PAMAM-*g*-diazirine(30mol%) samples (**4b**; compare orange bars for the samples following methanol extraction to blue bars for the unextracted samples). The amount of retained primer decreased with decreasing diazirine loading. For the PEI(25k)-*g*-diazirine(20wt%) samples (**4b**) an average of 68% of the primer was retained, and for the PEI(25k)-*g*-diazirine(10wt%) samples (**4c**) an average of 59% was retained. However, this analysis was complicated by the known[26,27] thermal decomposition of PEI, which leads to methanol-insoluble high-molecular weight aggregates. Thus, the PEI(25k) control (containing no diazirine) also retained 57% of added mass following heat activation and methanol extraction.

For the remaining two primers, we found that TETA-diazirine (**1**) was retained at an average of 83% of its initial impregnation mass, while PEI(800)-*g*-diazirine(30wt%) (**3a**) was retained at a lower level of only 22%, relative to the initial impregnation. Consistent with this result, we found that only 3% of the initial impregnation mass was retained in the PEI(800) control sample. Collectively, these data suggested that the desired C–H insertions were occurring to link the primer to the UHMWPE fiber surface, but that thermal background reactions for high-molecular weight polyamines were a complicating factor.

With primer-coated UHMWPE fabric in hand, we next turned to exploring the desired reaction with epoxy resin. Each sample of treated fabric was first cut into three *ca.* 100 mg portions

(to permit replicate analysis of epoxy loading) and then exposed to a methanolic solution of a commercial epoxy resin (West System Epoxy 105, with no added hardener). The sample was incubated at 110 °C for 16 h to facilitate the targeted nucleophilic addition reaction illustrated in Figure 1C, between surface-bound amines and electrophilic epoxide groups present in the epoxy resin. Following the reaction, each sample was extracted 3 times with methanol and 3 times with dichloromethane to remove any unreacted epoxy resin.

As expected, the vehicle control samples did not add any epoxy resin, and showed a small mass loss due to the extensive washing protocol removing soluble impurities from the UHMWPE fabric itself. By contrast, each of the samples that contained amines exhibited an increase in mass, resulting from epoxy that had reacted with the functionalized fiber surface. As shown in Figure 3A, the amount of reacted epoxy depended on the *type* of primer used in the loading experiment, as well as the *amount* of primer that had been added in the preceding step. PEI(25k)-*g*-diazirine(30wt%) samples (**4a**) gained an average amount of epoxy corresponding to 95% of the mass of added primer. In other words, for every milligram of primer added in the initial UHMWPE functionalization step, 0.95 mg of epoxy was bound to the surface in the subsequent nucleophilic addition step. The ratio increased for PEI(25k) primers that contained a higher level of free amines (i.e. those that had fewer nucleophilic positions blocked through the addition of diazirines). Thus, the PEI(25k)-*g*-diazirine(20wt%) samples (**4b**) gained an average of 119% epoxy, relative to the amount of primer, while the PEI(25k)-*g*-diazirine(10wt%) samples (**4c**) gained an average of 194%. Consistent with this trend, the PEI(25k) control sample, which contained insoluble polyamine aggregates resulting from thermal decomposition, accumulated 223% additional mass, relative to the amount of amine-containing material on the surface.

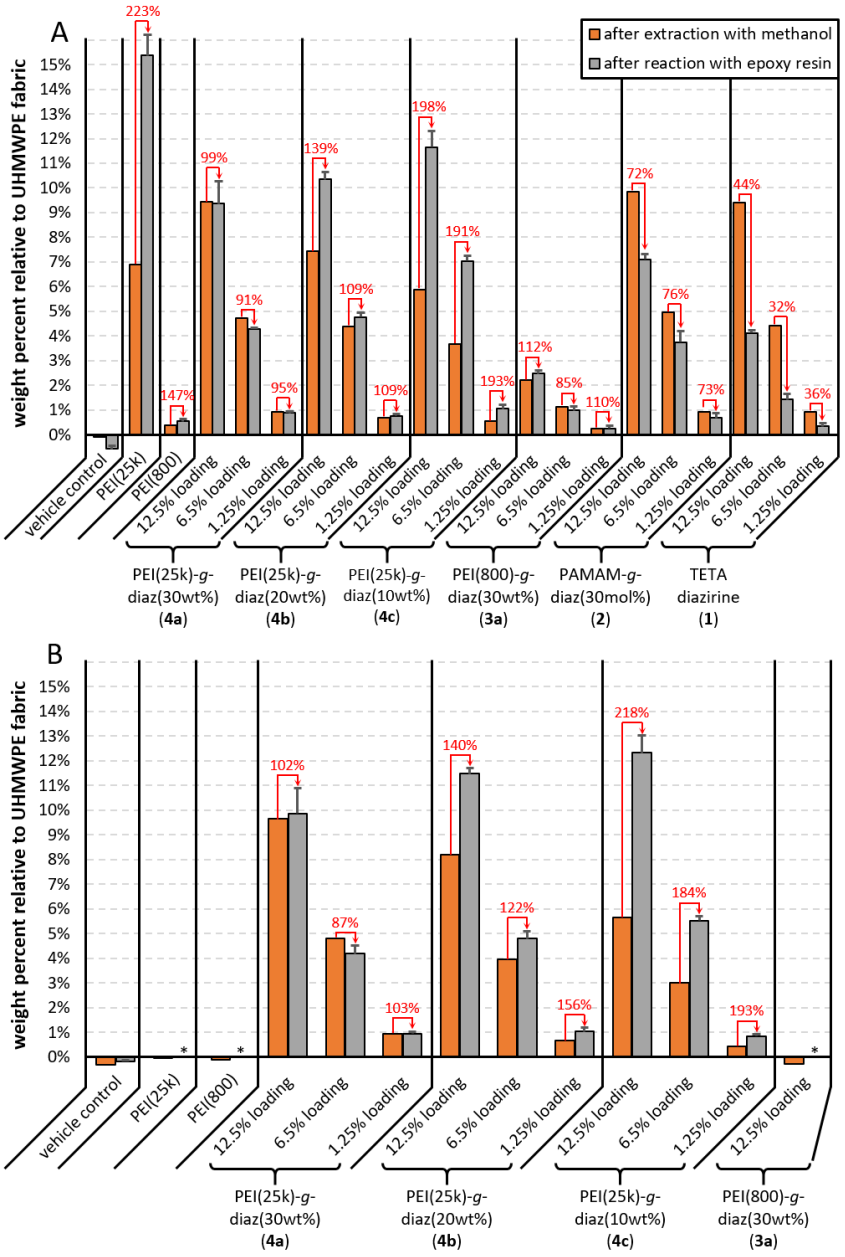


Figure 3. Reaction of epoxy resin on the surface of fabric loaded with polyamine–diazirine primers applied using thermal activation (panel A) and photochemical activation (panel B). For all experiments, the reaction of the epoxy with the amine-functionalized surface was carried out using thermal stimulation. Numbers in red indicate the weight percent of reacted epoxy, relative to the mass of loaded primer reagent. Asterisks indicate samples that contained no measurable amount

of primer and so were not carried forward to the epoxy treatment steps. Error bars indicate standard error over three replicates.

The other primers were also successful at reacting with epoxy resin, but each netted somewhat less total epoxy than the PEI(25k) primers—*either* due to a less-effective reaction between the surface-bound polyamine and the epoxy resin, *or* due to lower loading in the initial fiber functionalization step.

For example, PEI(800)-*g*-diazirine(30wt%) (**3a**) experienced a similar relative increase in mass (1.02 mg added epoxy for every mg of surface-bound primer) to the analogously functionalized PEI(25k)-*g*-diazirine(30wt%) (**4a**; 0.95 mg added epoxy per mg of primer)—but because much less of the smaller-molecular weight primer was attached to the surface in the initial immobilization step, the total amount of bound epoxy was much lower. By contrast, PAMAM-*g*-diazirine(30wt%) (**2**), for which similar loading levels to **4a** had been observed in the immobilization step (refer to the orange bars in Figure 2A and Figure 3A) was evidently less effective at reacting with available epoxy electrophile; an average of only 0.74 mg of epoxy was added for every mg of surface-bound primer **2**. TETA-diazirine **1** was even less effective, adding an average of only 0.37 mg of epoxy for every mg of surface-bound amine reagent.

The above data illustrate key structure–function relationships for our newly developed polyamine-diazirine primers. However, the results are once again complicated by the non-specific thermal degradation observed for PEI (and therefore for the PEI-diazirine conjugates as well), which resulted in the highest epoxy loading occurring for the PEI(25k) control sample.

In order to demonstrate primer adhesion and reaction with epoxy under conditions where thermal decomposition of PEI would not be a complicating factor, we turned to the use of

photochemical curing methods in the primer application step. Thus, primers **4a-c** as well as primer **3** and control polyamines PEI(25k) and PEI(800) were applied to the same woven 75 g/m^2 UHMWPE fabric as described above, but this time the samples were placed under a 365 nm light source for 16 hours instead of being incubated in an oven (refer to the Supporting Information for additional details around the choice of light source and the effect on curing time). The TETA-diazirine (**1**) and PAMAM-diazirine (**2**) primers were not used in these experiments, since our earlier measurements (*vide supra*) had shown that these were less successful at engaging in nucleophilic attack with epoxy resin.

The photochemical activation protocol resulted in a much cleaner surface functionalization of the UHMWPE fibers (Figure 2B). Both polyamine control samples—PEI(25k) and PEI(800)—showed no mass increase following washing, indicating that no insoluble polyamine aggregates were produced, and there was now a clear relationship between the degree of surface immobilization and the amount of diazirine present on the primer. PEI(25k)-*g*-diazirine(30wt%) (**4a**) was retained at an average level of 85%, while PEI(25k)-*g*-diazirine(20wt%) (**4b**) was retained at an average level of 64%, and PEI(25k)-*g*-diazirine(10wt%) (**4c**) was retained at an average level of 46%. Interestingly, the smaller-molecular weight PEI(800)-*g*-diazirine(30wt%) primer (**3a**) was not retained at all.

The above data are consistent with the average number of diazirines present per polymer molecule, and the known reactivity of the trifluoromethyl phenyl diazirine motif. In parallel work,[28] we found that the parent trifluoromethyl phenyl diazirine added to cyclohexane (a molecular model for polyethylene) in yields of only 35% following photochemical activation, and 15% following thermal activation. Much of the remaining mass balance was ketone that resulted from reaction of the intermediate triplet carbene with molecular oxygen. Given the lack of

selectivity for C–H insertion over side reactions (as well as the fact that generated carbenes can react with the polyamine backbone of the primer, at least as readily as they can with the desired UHMWPE fiber target), it stands to reason that in order to covalently link a polyamine to an UHMWPE fiber, one should ideally have several diazirine units present on each polymer chain. Otherwise the thermal or photochemical curing steps will result mostly in ketones or self-reaction products, and will not productively attach the primer to the surface.

Primer **3a** (PEI(800)-*g*-diazirine(30wt%)) incorporates an average of only 1.2 diazirine units per polymer chain (Table S2). As such, it is unsurprising that it does not bind efficiently to the UHMWPE surface. By contrast, primers **4c**, **4b**, and **4a** incorporate 10, 22, and 38 diazirines per polymer chain, respectively. It therefore makes intuitive sense that these three primers should function better in the immobilization step, and that the level of retained primer after washing should increase as one moves to higher diazirine loadings.

In addition to supporting a cleaner relationship between diazirine loading and immobilization, the UV-activated samples were also *physically* cleaner than the thermally activated samples, since they did not suffer from the yellowing that results from thermally promoted PEI degradation. As such, we were eager to study the epoxy uptake for these improved primer-coated UHMWPE materials.

The epoxy reaction protocol described above was repeated for the UV-activated samples. As shown in Figure 3B, we observed a clear increase in the amount of reacted epoxy as the number of available amine groups was increased across the series **4a** → **4b** → **4c**. Samples treated with PEI(25k)-*g*-diazirine(30wt%) (**4a**) gained an average of 0.98 mg epoxy for each mg of primer present on the surface of the fabric, while samples treated with PEI(25k)-*g*-diazirine(20wt%) (**4b**) gained an average of 1.39 mg epoxy for each mg of surface-bound primer. Most significantly,

samples treated with PEI(25k)-*g*-diazirine(10wt%) (**4c**) gained an average of 1.98 mg epoxy for every mg of primer. Once again, the vehicle control samples did not add any epoxy, and suffered a small mass loss due to the extensive solvent extraction process removing soluble impurities trapped within the commercial UHMWPE fabric.

The above data reveal an interesting trade-off between effective surface functionalization and effective nucleophilic addition reaction to the epoxy resin. Decreasing the number of diazirine units on the polymer chain (from **4a** to **4b** to **4c**) reduces the yield in the immobilization step, since fewer carbenes are generated that can participate in C–H insertion reactions. Primer **4c** therefore had the lowest percent retention of primer among the three PEI(25k)-diazirine reagents, while the PEI(25k) control sample did not retain any surface-bound reagent following UV activation. At the same time, lowering the diazirine loading effectively increases the number of amine groups that are available for nucleophilic addition with the electrophilic epoxy resin. Higher *relative* yields were therefore observed for **4c** over **4a**, in the epoxy reaction. Interestingly, although PEI(25k)-*g*-diazirine(10wt%) (**4c**) performed the worst among the three PEI(25k)-diazirine primers in the immobilization step, it actually bound the largest amount of total epoxy—up to 12.32wt% relative to the mass of the original UHMWPE fabric. This primer therefore emerged as our lead reagent for the preparation of polymer composite materials (*vide infra*).

3. Surface Characterization of Treated UHMWPE Fabrics

FT-IR spectra were recorded for representative UHMWPE fabrics treated with the various primers described above, using both thermal and photochemical activation for the primer attachment steps. In each case, spectra were recorded before and after reaction with epoxy resin, so that any changes could be documented.

For each set of samples (see Figures S13–S24 in the Supporting Information), the appearance of peaks corresponding to N–H stretching modes (*ca.* 3350 cm^{-1}) and N–H bending modes (*ca.* 1660 cm^{-1}) following primer application confirmed that the surface of the polymer had been successfully coated with amine groups. These signals greatly diminished when the primer-treated UHMWPE samples were allowed to react with epoxy resin, providing additional evidence that successful nucleophilic addition had taken place.

We were concerned that the amine-coated surfaces that were obtained following primer application might be oxidatively unstable, and so monitored representative primer-treated samples by FT-IR over time. As shown in Figures S25–S27, the amine signals persisted over a period of at least 16 days, suggesting that UHMWPE fabric treated in this way could have reasonable shelf stability.

For any given primer, no significant differences in the IR data were apparent when the activation mode was changed from thermal to photochemical excitation. Therefore, to gain further insight into local differences that may be present at the polymer surface when different activation methods were used, we conducted an extensive series of water contact-angle measurements to evaluate changes to surface hydrophobicity. Once again, we compared virgin UHWMPE fabric to samples that had been treated with various primers using both thermal and photochemical activation methods, and also examined changes that resulted from reaction of these treated surfaces with epoxy resin.

Interestingly (and in contrast to the FT-IR measurements discussed above), we observed substantial differences in contact angle depending upon the activation method used. When thermal activation was employed to attach the primer to the polymer surface, the measured contact angle never dropped below 90°, except in the case of the highest loading (12.5 wt%) of primer **4a** (Figure

S1A). For all other samples, only very modest decreases in hydrophobicity were observed, relative to that of the vehicle control sample. Reaction of the thermally applied polymer surfaces with epoxy resin did little to change this, and once again only in the case of the highest loading of primer **4a** did we observe a significant decrease in contact angle (Figure S1B). By contrast, photochemical application of the crosslinker dramatically improved hydrophilicity of the polymer fiber, to the point that in many cases (high and medium loadings of primers **4a** and **4b**, plus all three loading levels of primer **4c**) the water droplet was immediately drawn into the fiber, such that a contact angle of zero degrees was recorded for the experiment (Figure 4A). This effect was found to be highly reproducible. For each of the seven sample types in Figure 4A in which a contact angle of 0° was recorded, all ten water droplets applied to the treated surface exhibited identical behavior. When these highly polar surfaces were reacted with epoxy resin, the hydrophobicity increased in a dose-dependent fashion, such that the samples that had been treated with less primer recovered to a surface energy that was closer to that of the vehicle control (Figure 4B). Samples that had been treated with a higher primer loading retained a low contact angle following epoxy treatment, and in one case (a 12.5% loading of primer **4c**) remained sufficiently polar that the applied water droplet was drawn into the fiber faster than a contact angle could be recorded. Once again this behavior was found to be reproducible, with 10/10 droplets applied to different regions of the treated fabric surface exhibiting identical behavior.

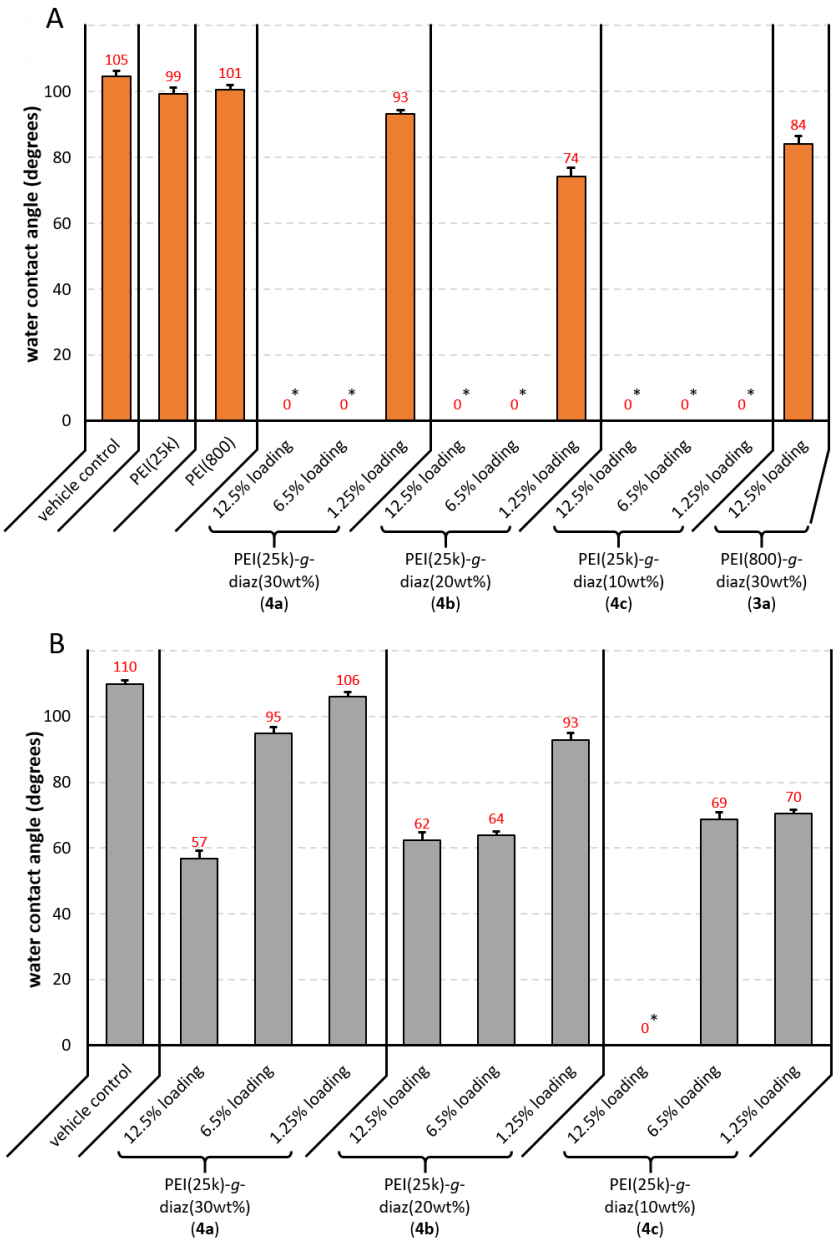


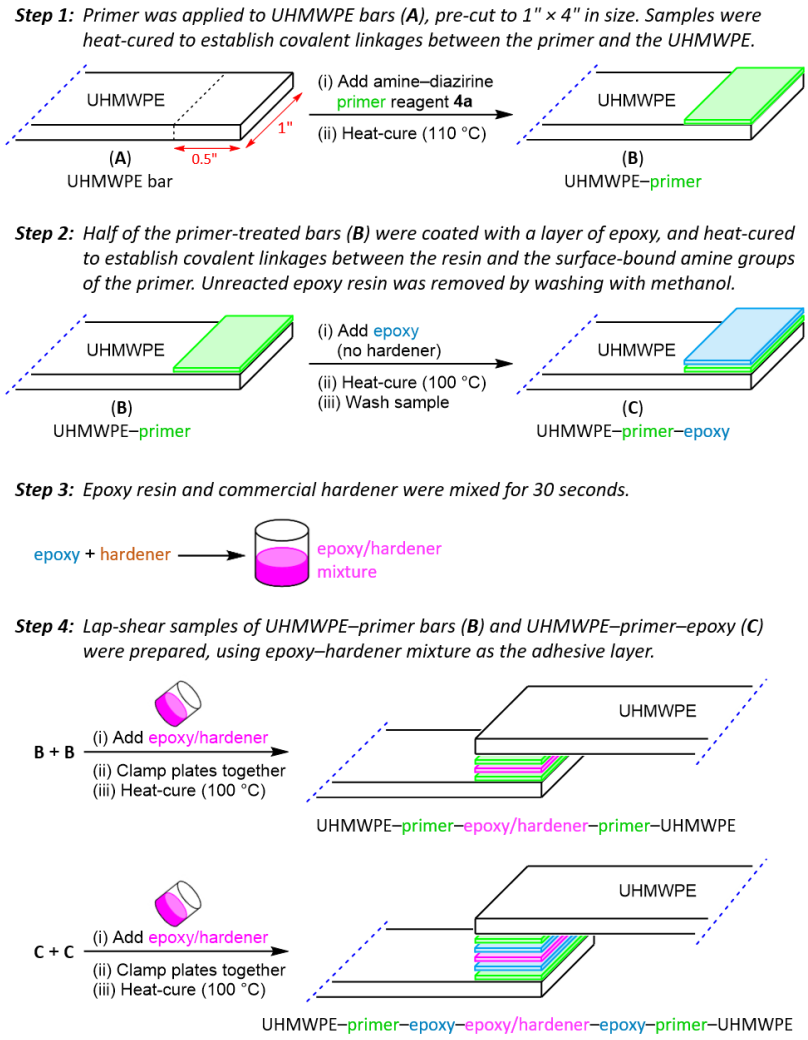
Figure 4. A: Average contact angle on UHMWPE surfaces to which the indicated primers were applied photochemically. B: Average contact angle for photochemically applied primer-coated surfaces reacted with epoxy resin. Orange bars indicate UHMWPE fabric samples that have been treated with primer and extracted with methanol; grey bars indicate samples that have been subsequently allowed to react with epoxy resin followed by further washing. Asterisks indicate that applied water droplets were immediately drawn into the treated fibers, such that a contact

angle of zero degrees was recorded. Error bars indicate standard error over ten replicates. Refer to Figure S1 for data from samples prepared using thermal activation of the primer.

4. Lap-Shear Experiments to Test UHMWPE–Epoxy Adhesion Strength

A successful fiber-reinforced composite requires that there be a strong adhesion between the fiber and the polymer matrix. To explicitly probe the adhesive force between primer-coated UHMWPE and epoxy resin, we constructed lap-shear samples from UHMWPE bars treated with PEI(25k)-*g*-diazirine(30wt%) (**4a**), using a mixture of epoxy resin and commercial hardener (West System 205) as the adhesant (refer to Scheme 2 for details of sample preparation). Positive controls included higher-surface energy materials—poly(methyl methacrylate) and aluminum metal—bonded using the same epoxy/hardener mixture (without the use of primer), to determine the maximum strength expected for the particular commercial epoxy system that was being used in our experiments.[29] Negative controls included untreated UHMWPE bars bonded with epoxy/hardener, to determine the effectiveness of epoxy for the virgin polyethylene material.

We were uncertain whether sufficient bonding would be achieved through the use of a single coat of primer, or whether a first layer of epoxy resin (i.e. an initial epoxy 'sizing') would need to be covalently linked to the surface (as in the fabric experiments described in Figure 3) to provide a network suitable for interaction with the epoxy/hardener mixture. We therefore prepared lap-shear samples from simple primer-treated bars (i.e. **B**+**B**, Scheme 2) as well as samples from primer-treated UHMWPE that had been initially reacted ('sized') with epoxy resin (i.e. **C**+**C**, Scheme 2).



Scheme 2. Workflow for preparation of lap-shear samples from UHMWPE bars treated with primer **4a**. Control samples are not illustrated, but are referred to in the text and in Figure 5.

To measure the adhesion strength, each sample was pulled laterally at 3 mm/min until failure, and the force required to break the joint (divided by the 0.5 in^2 area used for the overlap region) was plotted in Figure 5. The data indicated that negative control samples (i.e. UHMWPE bars bonded with the epoxy/hardener mixture) displayed low adhesion strengths of *ca.* 0.67 MPa, as expected for a low surface energy material (refer to Figure S2 for the effect of different

epoxy/hardener loadings on adhesion strength for these negative control samples). By contrast, positive control samples (i.e. aluminum–epoxy/hardener–aluminum or PMMA–epoxy/hardener–PMMA) showed higher adhesion strengths of *ca.* 2 MPa.

UHMWPE bars that had been treated with primer **4a** (or with **4a** and an epoxy sizing) prior to application of the epoxy/hardener mixture showed significantly increased adhesion relative to the negative control samples. In fact the adhesion strength exceeded that of the positive controls,[29] reaching *ca.* 2.5 MPa. This is less adhesion than we previously observed by installing chemical crosslinks between polyethylene bars,[11(b)] but is similar to polymer oxidation methods that are known to result in strong adhesive bonding for polyethylene.[30]

Interestingly, we found only modest differences in adhesion strength when we added 0.5 or 1.0 mg of primer to each UHMWPE bar (compare the hashed vs. solid bars in Figure 5 and Figure S2), and no significant differences with or without the use of an epoxy sizing (compare the blue vs. green bars in Figure 5 and Figure S2). In contrast to the negative control samples, which gave better adhesion with larger amounts of applied adhesant, we also found no significant difference in adhesion when we altered the level of epoxy/hardener mixture applied to the bars (see Figure S2). This consistency of adhesion suggests that failure is occurring—at least partially—within the epoxy matrix, rather than at the interface.[31]

We also briefly examined the use of PEI(25k) in place of PEI(25k)-*g*-diazirine(10wt%) (**4a**). While the earlier experiments with UHMWPE fabric (*vide supra*) indicated that thermally decomposed PEI is difficult to remove from the surface, the adhesion experiments clearly showed reduced bonding when the non-diazirine material was used as the primer (compare grey bars vs. green bars in Figure 5). These data indicate that even under thermal activation conditions the

diazirine groups are still playing an important role in facilitating bonding to the surface of the UHMWPE.

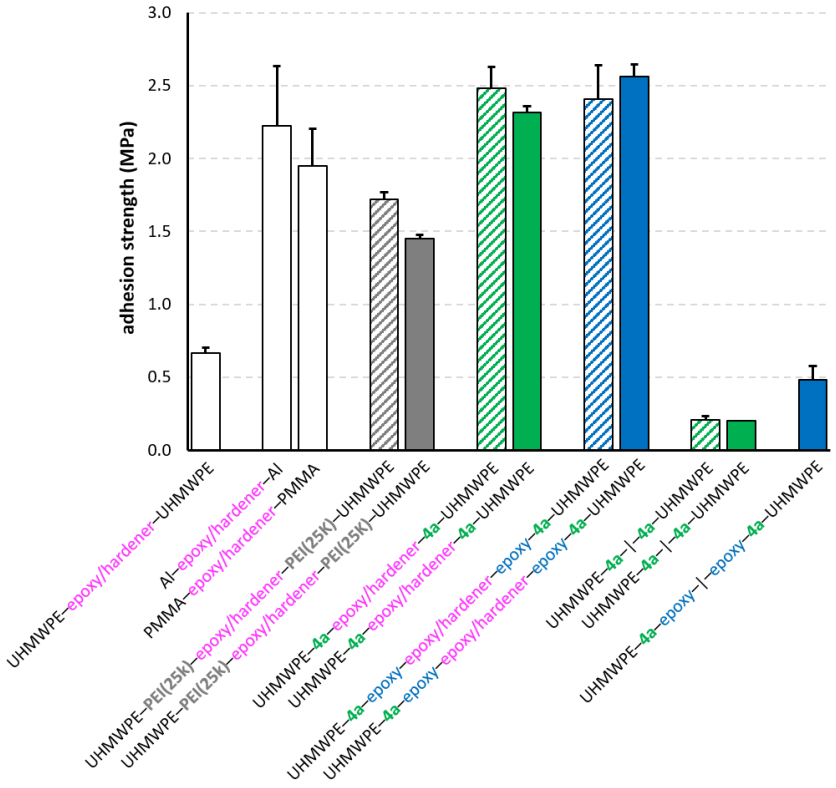


Figure 5. Measured adhesion strength for lap-shear samples, following bonding with 10 mg or 0 mg of the epoxy/hardener mixture. White bars = no primer used. Grey bars = application of PEI. Green bars = application of primer **4a** (PEI(25k)-*g*-diazirine(30wt%)). Blue bars = application of primer **4a**, followed by epoxy sizing. Hashed bars = 0.5 mg primer applied in the 1" × 0.5" contact region of each UHMWPE bar. Solid bars = 1.0 mg primer applied in the 1" × 0.5" contact region of each UHMWPE bar. The | symbol indicates a vehicle control sample in which no epoxy/hardener mixture was added. Error bars indicate standard error. Refer to Table S8 for numbers of replicates used for each test condition. See Figure S2 for lap-shear data using different amounts of epoxy/hardener mixture.

Only minimal adhesion (i.e. less than in the negative control) was observed when the epoxy/hardener mixture was left out, and the two primer-coated bars (B or C) were simply clamped together and heated (refer to the last three bars on the far right of Figure 5). This minimal level of adhesive bonding is presumably due to the fact that the two primer-treated surfaces display a relatively high local surface energy, as a result of the attached amine groups (vide supra).

The data in Figure 5 strongly suggest the existence of a covalent network between the epoxy matrix and the primer that is covalently bound to the UHMWPE surface. In order to confirm the presence of this network (by ruling out the possibility that a simple increase to the substrate polymer's surface energy is responsible for improved adhesion) we carried out one final experiment in which the hardener reagent was left out of the adhesant layer. Specifically, a layer of epoxy (with no hardener) was sandwiched between two UHMWPE bars that had each been pre-treated with 1.0 mg of **4a**, and the resulting lap-shear sample was thermally cured for the same amount of time that had been used for the epoxy/hardener samples described above. Testing revealed an adhesion strength of 1.11 ± 0.06 MPa—less than the 2.5 MPa observed for the test samples in Figure 5, but much more than the 0.2 MPa measured in the primer controls. Because epoxy resin itself (i.e. in the absence of hardener) is a poor adhesive, this result unambiguously confirms the existence of covalent bonds between the epoxy and the amine-treated surface.

5. Epoxy Infusion and 3-Point Bending Tests

In order to evaluate the effect of the optimized polyamine–diazirine primer upon subsequent composite material manufacturing and performance metrics, we coated > 4.7 m^2 of UHMWPE fabric with nominal loadings of either 0 or 1 wt% of primer **4c** (PEI(25k)-*g*-diazirine(10wt%)). Diazirine activation in primer-impregnated samples was accomplished

thermally (110 °C for 4 hours) or photochemically (365 nm for 16 hours), after which the fabric was extracted three times with methanol to remove unbound primer. Half of the primer-treated samples were then further reacted with epoxy (110 °C for 16 hours) and then washed three times with methanol and three times with dichloromethane to remove any resin that was not covalently linked to the surface. Each piece of fabric was weighed at multiple steps throughout the process to ensure that the expected amounts of primer and/or epoxy sizing were successfully added at each stage.

Vehicle control fabrics, primer-treated fabrics, and primer-and-epoxy-treated fabrics were then assembled into 30-layer stacks of fabric 12 cm long x 12 cm wide, in a vacuum-bag resin-infusion apparatus. A commercial epoxy/hardener mixture suitable for the manufacture of high-performance composites (Rhino 1411/4111) was applied under constant vacuum, and the impregnation of the resin into the fabric was monitored over time, in order to assess the effective permeability of the fabric to the epoxy/hardener mixture. For each composite sample, the volume-fraction of fiber was set to 48% ± 2%.

The permeability of the primer-treated samples was found to be significantly higher than those of the vehicle control samples (Figure 6). Samples in which an initial layer of chemically bound epoxy resin had been added to the epoxy prior to infusion had an even greater permeability.

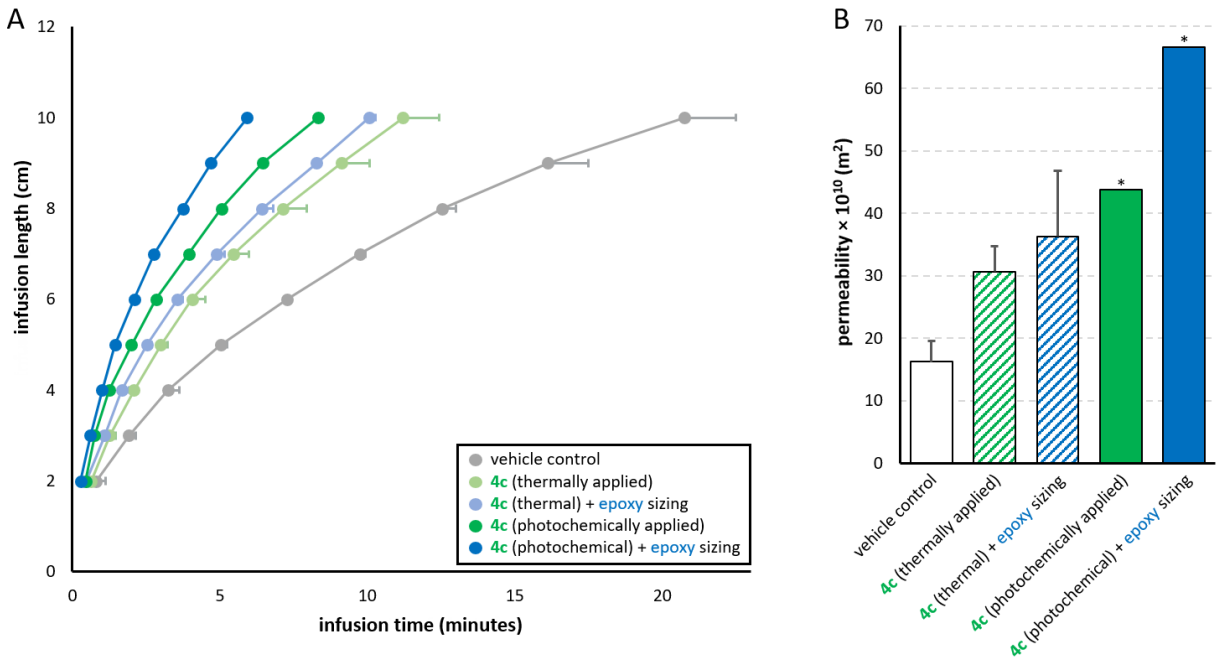


Figure 6. Infusion data for epoxy–UHMWPE layups. A: comparison of average infusion length (when filling a 12 cm x 12 cm sample) vs. time data for UHMWPE fabrics with different surface treatments. B: comparison of calculated permeability values. White bars = no primer used. Green bars = application of primer **4c** (PEI(25k)-*g*-diazirine(10wt%)). Blue bars = application of primer **4c**, followed by epoxy sizing. Hashed bars = thermal activation of primer. Solid bars = UV activation of primer. Error bars indicate standard deviation for measurements made on the second and third infusions; the first run in each case was used to establish infusion parameters and so was not included in the analysis. Asterisks indicate that singleton samples were used, due to physical limitations in the UV curing apparatus.

The permeability of a fabric is a measure of how rapidly a fluid of defined viscosity (in this case epoxy resin) can be drawn through the material, under the application of a given pressure differential. Because the applied macroscopic pressure drop was constant for the five types of samples compared in Figure 6, the dramatic difference in filling performance is attributable

entirely to differences in microscopic capillary forces between the surface of the treated or untreated UHMWPE fiber and the resin/hardener mixture. Consistent with our initial hypothesis, the presence of the chemically bound polyamine primer evidently makes the UHMWPE fabric surface more accommodating to the applied epoxy resin, resulting in a much larger observed flow rate (relative to vehicle control samples) and a higher permeability. Covalent linking of an initial epoxy layer onto the primer-treated surface further improves the affinity of the surface for the epoxy/hardener mixture. Consistent with our earlier contact angle measurements, UV activation of the primer further enhances this interaction between the surface and the resin, relative to thermal activation—with or without the use of an epoxy sizing step. However, direct statistical comparisons between thermal activation and photochemical activation methods cannot be made, since size limitations on our laboratory's UV chamber limited the number of treated UHMWPE layers that could be produced.

The various epoxy/UHMWPE composite materials described above were post-cured according to the resin manufacturer's recommended cure cycle (4 hours at 65 °C followed by 2 hours at 85 °C), and then rectangular samples were cut from each material for mechanical testing using a standard 3-point bending experiment (ASTM D2344).[32,33] As shown in Figure 7, we observed consistent mechanical strength for composite materials prepared from unmodified UHMWPE or from vehicle control fabrics that had been exposed to our dispersal solvents and heating conditions, but where no primer was added. Interestingly, however—and once again in keeping with our central hypothesis—the altered surface chemistry achievable using polyamine–diazirine **4c** was shown to affect the mechanical strength of the composite.

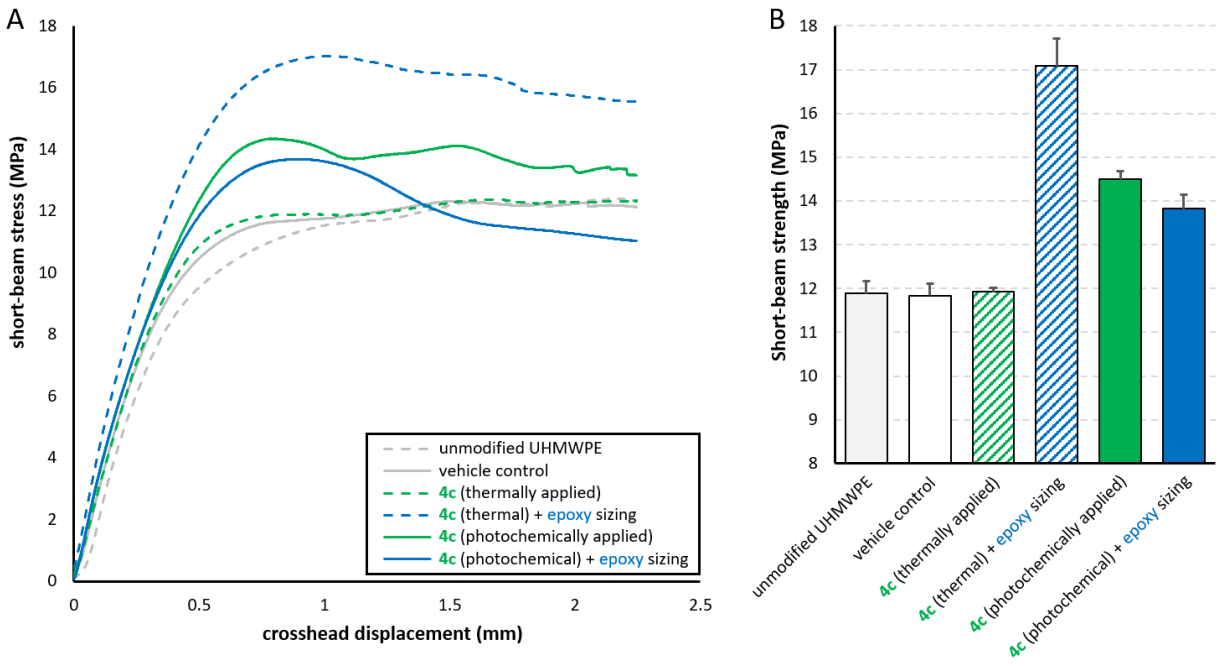


Figure 7. Mechanical testing data using epoxy–UHMWPE composite materials. A: averaged short beam shear stress vs. crosshead displacement curves for composite materials derived from UHMWPE fabrics with different surface treatments. B: comparison of average shear strength measured for each sample type. White and grey bars = no primer used. Green bars = application of primer **4c** (PEI(25k)-*g*-diazirine(10wt%)). Blue bars = application of primer **4c**, followed by epoxy sizing. Hashed bars = thermal activation of primer. Solid bars = UV activation of primer. Error bars indicate standard error. Refer to Table S11 for numbers of replicates used for each test condition.

While the measured short-beam strength remained modest for all samples (< 20 MPa), significant differences were found depending upon the surface treatment that was used. Thermal application of primer **4c** resulted in no improvement to mechanical strength relative to control samples (perhaps because the presence of poorly bound polymer aggregates from thermally

induced PEI degradation counteracts the beneficial effects of the primer), but clear improvements were seen by either using a photochemical activation method in place of thermal activation or else by adding an epoxy sizing. Interestingly, the addition of a covalently bound layer of epoxy does not improve the performance of composite materials derived from primer-coated UHMWPE where the primer was applied photochemically, while the application of epoxy sizing to fabric that had gone through a thermal primer-coating step provided the best overall performance. These differences are likely attributable to the aggregation state of the polyamine; detailed characterization of these aggregates is beyond the scope of the present study.

All UHMWPE–epoxy composites underwent inelastic deformation as a result of the 3-point bending experiment (Figure S33), rather than the brittle failure that would be expected for a similarly constructed fiberglass–epoxy or carbon-fiber–epoxy composite.[34,35] The lack of brittle failure in these samples highlights the potential utility of UHMWPE–composite materials for applications where mechanical fracture must be avoided.

CONCLUSION

The data presented herein indicate a role for polyamine–diazirine conjugates as a bridge between UHMWPE fibers (and likely other low-functionality polyolefins) and epoxy resin. Our results indicate the establishment of a covalent network extending from the polyethylene fiber through the chemically bound primer reagent and into the epoxy matrix (refer to the Supplemental Information for additional ^{1}H NMR, IR, and elemental analysis data that support the formation of specific covalent bonds between the polyamine conjugate and the aliphatic substrate). This covalent network is sufficient to support significant adhesive forces between the fiber surface and

the cured resin, and is able to improve the mechanical properties of manufactured UHMWPE–epoxy composite materials.

Other groups have already shown that functionalization of UHMWPE fibers with polyamine coatings improve their ability to participate in epoxy-based composites. For example, the Feng and Zhao laboratory[36] showed that a polydopamine coating[37] that was further functionalized through grafting of 1,6-diaminohexane (hexamethylenediamine) improved interfacial shear strength between the fiber and the matrix by over 80% (relative to that of pristine UHMWPE fibers), without negatively affecting the ultimate tensile strength of the fibers themselves.[36] However, previous methods to achieve these benefits have either made use of non-covalent coatings (which may be prone to delamination) or have required the production of bespoke polyethylene copolymers (which come with added production challenges). The use of polyamine–diazirine conjugates as primers represents a third option that combines the convenience of a topical application system with the strong adhesive forces resulting from installation of robust covalent bonds to the UHMWPE fiber.

ASSOCIATED CONTENT

Supplemental figures and tables, complete experimental details, numerical data used to create the plots, ^{1}H, ^{13}C and FTIR spectra, supplemental photos and images (PDF).

AUTHOR INFORMATION

Corresponding Author

Jeremy E. Wulff – *Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada; Centre for Advanced Materials and Related Technology (CAMTEC),*

University of Victoria, Victoria, British Columbia V8P 5C2, Canada; orcid.org/0000-0001-9670-160X;

Email: wulff@uvic.ca

Authors

Rashid Nazir – *Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada;* orcid.org/0000-0002-2673-9925

Liting Bi – *Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada;* orcid.org/0000-0003-3361-5338

Stefania F. Musolino – *Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada;* orcid.org/0000-0002-0990-1855

Olivia H. Margoto – *Composites Research Network (CRN), University of British Columbia, Kelowna, British Columbia V1V 1V7, Canada;* orcid.org/0000-0002-8154-1495

Kuthan Çelebi – *Composites Research Network (CRN), University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada;* 0000-0003-3288-8780

Christophe Mobuchon – *Composites Research Network (CRN), University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada*

Mahdi Takaffoli – *Materials and Manufacturing Research Institute (MMRI), University of British Columbia, Kelowna, British Columbia V1V 1V7, Canada;* orcid.org/0000-0002-2348-2562

Abbas S. Milani – *Materials and Manufacturing Research Institute (MMRI), University of British Columbia, Kelowna, British Columbia V1V 1V7, Canada;* orcid.org/0000-0003-1173-9989

Greg Falck – *Aluula Composites, Victoria, British Columbia V8Z 1T3, Canada*

Author Contributions

J.W. and G.F. conceived the study. Polyamine–diazirine conjugates **1**–**4** were synthesized by L.B., S.M., and R.N. Fabric testing described in Figures 2 and 3 was carried out by R.N., as was interrogation of fabric surface chemistry (Figure 4 and Figure S1). Lap-shear samples were prepared by L.B. and analyzed by O.H., working under the guidance of M.T. and A.M. Composite materials were prepared and tested by K.Ç., working under the supervision of C.M. The manuscript was written by J.W. with the input of all authors.

Conflict of Interest Disclosure

The authors declare the following competing financial interest(s): J.W., S.F.M., R.N. and L.B. are co-inventors on patent application 63/158,578, which claims the use of the epoxy primers described herein. There are no additional conflicts to declare.

ACKNOWLEDGMENT

We gratefully acknowledge funding from Innovate BC (grant 184-RND8-2019). L.B. and S.F.M. additionally thank Mitacs Canada (grants IT11982 and IT17318) for fellowships, and J.W. thanks the Canada Research Chairs program (file number 950-231376) for salary support.

ABBREVIATIONS

CCR2, CC chemokine receptor 2; CCL2, CC chemokine ligand 2; CCR5, CC chemokine receptor 5; TLC, thin layer chromatography.

REFERENCES

1. Wazalwar, R.; Sahu, M.; Raichur, A. M. Mechanical properties of aerospace epoxy composites reinforced with 2D nano-fillers: current status and road to industrialization. *Nanoscale Adv.* **2021**, *3*, 2741.

2. Patel, M.; Pardhi, B.; Chopara, S.; Pal, M. Lightweight composite materials for automotive - a review. *Int. Res. J. Eng. Technol.* **2018**, *5*, 41–47.

3. Yudhanto, A.; Alfano, M.; Lubineau, G. Surface preparation strategies in secondary bonded thermoset-based composite materials: A review. *Composites Part A* **2021**, *147*, 106443.

4. Ilankeeran, P. K.; Mohite, P. M.; Kamle, S. Axial tensile testing of single fibres. *Mod. Mech. Eng.* **2012**, *2*, 151–156.

5. Minus, M. L.; Kumar, S. The processing, properties, and structure of carbon fibers. *JOM* **2005**, *57*, 52–58.

6. Lau, K.; Hung, P.; Zhu, M.-H.; Hui, D. Properties of natural fibre composites for structural engineering applications. *Composites Part B* **2018**, *136*, 222–233.

7. van der Werff, H.; Heisserer, U. High-performance ballistic fibers: ultra-high molecular weight polyethylene (UHMWPE). In Advanced Fibrous Composite Materials for Ballistic Protection. Chen, X., Ed. 2016, pp. 71–107.

8. (a) Sanborn, B.; DiLeonardi, A. M.; Weerasooriya, T. Tensile Properties of Dyneema SK76 Single Fibers at Multiple Loading Rates Using a Direct Gripping Method. Army Research Laboratory Report 2014, ARL-TR-6974; (b) Ultra High Molecular Weight Polyethylene Fiber from DSM Dyneema. DSM Technical Report 2016, CIS YA100.

9. Chhetri, S.; Bougherara, H. A comprehensive review on surface modification of UHMWPE fiber and interfacial properties. *Composites Part A* **2021**, *140*, 106146.

10. Li, W.; Feng, M.; Liu, X.; Huang, M.; Ma, R. Ultra-high molecular weight polyethylene fibers/epoxy composites: effect of fiber treatment on properties. *Fibers and Polymers* **2019**, *20*, 421–427.

11. (a) Lepage, M. L.; Simhadri, C.; Liu, C.; Takaffoli, M.; Bi, L.; Crawford, B.; Milani, A. S.; Wulff, J. E. A broadly applicable cross-linker for aliphatic polymers containing C–H bonds. *Science* **2019**, *366*, 875–878; (b) Simhadri, C.; Bi, L.; Lepage, M. L.; Takaffoli, M.; Pei, Z.; Musolino, S. F.; Milani, A. S.; Dilabio, G. A.; Wulff, J. E. Flexible polyfluorinated bis-diazirines as molecular adhesives. *Chemical Science* **2021**, *12*, 4147–4153; (c) Cuthbert, T. J.; Ennis, S.; Musolino, S. F.; Buckley, H. L.; Niikura, M.; Wulff, J. E.; Menon, C. Covalent functionalization of melt-blown polypropylene filters with diazirine–photosensitizer conjugates producing visible light driven virus inactivating materials. *Scientific Reports* **2021**, *11*, 19029.

12. Burgoon, H.; Cyrus, C.; Skilskyj, D.; Thoresen, J.; Ebner, C.; Meyer, G. A.; Filson, P.; Rhodes, L. F.; Backlund, T.; Meneau, A.; Cull, T.; Afonina, I. Photopatterning of low dielectric constant cycloolefin polymers using azides and diazirines. *ACS Appl. Polym. Mater.* **2020**, *2*, 1819–1826.

13. (a) Dey, K.; Chowdhury, S. R.; Dykstra, E.; Koronatov, A.; Lu, H. P.; Shinar, R.; Shinar, J.; Anzenbacher, P. Diazirine-based photo-crosslinkers for defect free fabrication of solution processed organic light-emitting diodes. *J. Mater. Chem. C* **2020**, *8*, 11988–11996; Dey, K.; Chowdhury, S. R.; Dykstra, E.; Lu, H. P.; Shinar, R.; Shinar J.; Anzenbacher, P. Effect of bis-

diazirine-mediated photo-crosslinking on polyvinylcarbazole and solution-processed Polymer LEDs. *ACS Appl. Electron. Mater.* **2021**, *3*, 3365–3371.

14. Wu, C.; Li, C.; Yu, X.; Chen, L.; Gao, C.; Zhang, X.; Zhang, G.; Zhang, D. An efficient diazirine-based four-armed cross-linker for photo-patterning of polymeric semiconductors. *Angew. Chem. Int. Ed.* **2021**, *60*, 21521–21528.

15. Jiang, H.; Guo, G.; Chen, W.; Cui, Z. Reactive dyeing of synthetic fibers employing dyes containing a diazirine moiety. *Dyes Pigm.* **2021**, *194*, 109555.

16. Zheng, Y.-Q.; Liu, Y.; Zhong, D.; Nikzad, S.; Liu, S.; Yu, Z.; Liu, D.; Wu, H.-C.; Zhu, C.; Li, J.; Tran, H.; Tok, J. B.-H.; Bao, Z. Monolithic optical microlithography of high-density elastic circuits. *Science* **2021**, *373*, 88–94.

17. Brunner, J.; Senn H.; Richards, F. M. 3-Trifluoromethyl-3-phenyldiazirine. A new carbene generating group for photolabeling reagents. *J. Biol. Chem.* **1980**, *255*, 3313–3318.

18 . Tan, N. C. S.; Djordjevic, I.; Malley, J. A.; Kwang, A. L. Q.; Ikhwan, S.; Šolić, I.; Singh, J.; Wicaksono, G.; Lim, S.; Steele, T. W. J. Sunlight activated film forming adhesive polymers. *Mater. Sci. Eng. C* **2021**, *127*, 112240.

19. (a) Ping, J.; Gao, F.; Chen, J. L.; Webster, R. D.; Steele, T. W. J. Adhesive curing through low-voltage activation. *Nat. Commun.* **2015**, *6*, 8050–8058; (b) Singh, M.; Webster, R. D.; Steele, T. W. J. Voltaglue Electroceutical Adhesive Patches for Localized Voltage Stimulation. *ACS Appl. Bio Mater.* **2019**, *2*, 2633–2642; (c) Singh, M.; Yin, C. S.; Page, S. J.; Liu, Y.; Wicaksono, G.; Pujar, R.; Choudhary, S. K.; Kulkarni, G. U.; Chen, J.; Hanna, J. V.; Webster, R. D.; Steele, T. W.

J. Synergistic voltaglue adhesive mechanisms with alternating electric fields. *Chem. Mater.* **2020**, *32*, 2440–2449.

20. Geri, J. B.; Oakley, J. V.; Reyes-Robles, T.; Wang, T.; McCarver, S. J.; White, C. H.; Rodriguez-Rivera, F. P.; Parker, D. L. Jr.; Hett, E. C.; Fadeyi, O. O.; Oslund, R. C.; MacMillan, D. W. C. Microenvironment mapping via Dexter energy transfer on immune cells. *Science*, **2020**, *367*, 1091–1097.

21. Djordjevic, I.; Wicaksono, G.; Šolić, I.; Singh, J.; Sushil Kaku, T.; Lim, S.; Ang, E. W. J.; Blancafort, L.; Steele, T. W. J. Rapid Activation of Diazirine Biomaterials with the Blue Light Photocatalyst. *ACS Appl. Mater. Interfaces* **2021**, *13*, 36839–36848.

22. Zhang, L.; Ou, Y.; Wang, D.-Y. Surface functionalization of carbon fabric towards high-performance epoxy composites via enhanced fiber–matrix interfacial strength and intergrowth charring behavior. *Express Polym. Lett.* **2021**, *15,* 503–514.

23. (a) Zhang, X.; Sun, T.; Lei, Y.; Liang, M.; Zou, H. Synergistically optimizing interlaminar behavior of CFRP composites by simultaneously applying amino-rich graphene oxide to carbon fiber and epoxy matrix. *Composites Part A* **2021**, *145*, 106372; (b) Shen, L.; Zhang, X.; Lei, Y.; Liang, M.; Chen, Y.; Chen, W.; Zou, H. Efficient reinforcement of epoxy resin with amine-rich rigid short-chain grafted graphene oxide. *Polymer Composites* **2021**. Ahead of print.

24. Gharieh, A.; Moghadas, M.; Pourghasem, M. Synergistic effects of acrylic/silica armored structured nanoparticles on the toughness and physicomechanical properties of epoxy polymers. *ACS Applied Polymer Materials* **2021**, *3*, 4008–4016.

25. Similar PEI diazirines were prepared used by Hatanaka and co-workers for use in immobilizing enzymes. See: Tomohiro, T.; Tachi, N.; Azuma, Y.; Hatanaka, Y. Hydrophilic diazirine polymer for one-step photo-fabrication of proteins on polypropylene surface. *Heterocycles* **2009**, 897–908.

26. Nedel'ko, V. V.; Korsunskii, B. L.; Dubovitskii, F. I.; Gromova, G. L. The thermal degradation of branched polyethylenimine. *Vysokomol. Soyed.* **1975**, *17*, 1477–1481.

27. Idris, S. A.; Mkhatresh, O. A.; Heatley, F. Assignment of ^{1}H NMR spectrum and investigation of oxidative degradation of poly(ethylenimine) using ^{1}H and ^{13}C 1-D and 2-D NMR. *Polym. Int.* **2006**, *55*, 1040–1048.

28. Musolino, S. F.; Pei, Z.; Bi, L.; DiLabio, G. A.; Wulff, J. E. Structure–function relationships in aryl diazirines reveal optimal design features to maximize C–H insertion. *Chemical Science* **2021**, *12*, 12138–12148.

29. Imaging of the aluminum–epoxy/hardener–aluminum control sample after lap-shear testing (see Figures S28–S29) indicates that the sample suffered adhesive failure, which likely explains why this intended positive control yielded a lower adhesion strength than our test samples. Likewise, we have previously shown (see reference 11b) that adhesively bonded PMMA samples are prone to substrate failure.

30. (a) Musolino, S. F.; Wulff, J. E. Catalytic C–H oxidation enhances polyethylene bonding. *Chem* **2021**, *7*, 7–9; (b) Chen, L.; Malollari, K. G.; Uliana, A.; Sanchez, D.; Messersmith P. B.; Hartwig, J. F. Selective, catalytic oxidations of C–H bonds in polyethylenes produce functional materials with enhanced adhesion. *Chem* **2021**, *7*, 137–145.

31. Attempts to confirm cohesive failure within the lap-shear samples was thwarted by surface deformations in the UHMWPE substrate, which occurred as a result of the large forces exerted during the experiment; refer to the Supporting Information (Figures S30–S31) for further details and representative laser interferometry measurements.

32. ASTM Standard D 2344/D 2344M-00. Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates. ASTM International (W. Conshohocken, PA).

33. Adams, D. F.; Lewis, E. Q. Experimental Study of Three- and Four-Point Shear Test Specimens. *J. Compos. Tech. Res.* **1995**, *17*, 341–349.

34. Aslan, Z. Apparent Interlaminar Shear Strength Measurement by Four Point Short Beam Test. *Adv. Compos. Lett.* **2015**, *24*, 27–32.

35. Alsaadi, M.; Ugla, A. A.; Erklig, A. A comparative study on the interlaminar shear strength of carbon, glass, and Kevlar fabric/epoxy laminates filled with SiC particles. *J. Compos. Mater.* **2017**, *51*, 2835–2844.

36. Hu, J.; Feng, X.; Liu, Z.; Zhao, Y.; Chen, L. Surface amine-functionalization of UHMWPE fiber by bio-inspired polydopamine and grafted hexamethylene diamine. *Surf. Interface Anal.* **2017**, *49*, 640–646.

37. Hong, S.; Na, Y. S.; Choi, S.; Song, I. T.; Kim, W. Y.; Lee, H. Non-covalent self-assembly and covalent polymerization co-contribute to polydopamine formation. *Adv. Funct. Mater.* **2012**, *22*, 4711–4717.