# Surface Modification and Dyeing of Ultra-high-molecular-weight Polyethylene Fabrics using Diazirine-Based Polymers

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2024

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KEYWORDS: UHMWPE, diazirines, crosslinking, primers, dyes.

ABSTRACT: Ultra-high-molecular weight polyethylene (UHMWPE) fibers are valued for their high strength-to-weight ratio and are employed in a wide variety of commercial applications. However, because of its low surface energy, UHMWPE can fail in certain applications, such as fiber-reinforced composites. This is due to its poor interfacial adhesion with polar matrices, making it challenging to incorporate into composites and/or retain polar dyes or colorants. Herein, we describe the use of polyamine primers for coating UHMWPE weaves, covalently bonding the aliphatic chains through C−H insertion, leading to strong covalent interactions between fabric and polyamines. We further demonstrate that the polyamine-coated UHMWPE surfaces can successfully react with epoxy resin through nucleophilic addition reactions to enable the

production of epoxy composites. Furthermore, we show the use of polyamine-coated UHMWPE in secondary functionalization with amine-reactive compounds, such as dyes, through covalent linkages that result in very strong color fastness.

## INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) fabrics and composites are highly sought after in various industrial applications, including automotive, aerospace, defense armor and medical device manufacturing.[1-5] UHMWPE is known for its extremely high toughness, high strength-to-weight ratio, excellent wear resistance, low coefficient of friction, and good chemical resistance. It is a particularly good material for resisting high-velocity impact and is ideal for high-performance and durable applications.[5] Additionally, the biocompatibility of UHMWPE materials allows for their use in medical implants and prosthetics. As a result of these qualities, the demand for UHMWPE fabrics and composites is expected to continue to grow in the coming years. Although it is rising in popularity, UHMWPE is a very low surface energy material with a high degree of crystallinity, and it lacks suitable functional groups and polar moieties to permit chemical interactions with other materials.[6-9] For example, creating high-quality composites with lipophilic UHMWPE fibers can be challenging, as achieving optimal bonding with high surface energy epoxy resins is difficult due to the inherent weakness of the interaction between the two dissimilar materials.[9-11] The lack of interfacial adhesion between resin and reinforcing fibers prevents the efficient transfer of force between layers. Physical or chemical surface modifications can enhance adhesion but at the expense of the integrity of the strength of the virgin fiber chains.[9] Expensive and destructive surface treatments, such as corona discharge, plasma treatment,[12,13] or exposure to harsh chemical oxidants, oxidize the polyethylene surface and favor its binding with the desired

substrates.[9,14-16] These approaches offer improved adhesion between the polyethylene fiber and the polymer matrix;[10] however, they cause chain fragmentations and other side processes that affect fiber integrity.[17] Milder surface treatment methods include the use of secondary polymer coatings, for example, polydopamine,[6,18] or embedding nanofillers within the polymer fibers using carbon nanotubes or nanoclays.[19] However, these approaches do not lead to the formation of covalent bonds between the coating and the UHMWPE fiber, which can result in slippage or adhesion failure. An alternative approach is to use chemical reagents that can functionalize UHMWPE fabric through carbene insertion, forming strong covalent bonds. This process involves forming high-energy carbenes, which insert into the inert C−H bonds present on UHMWPE fiber chains and result from thermal activation (temperatures higher than 80 °C)[20] or photochemical activation (at wavelengths of 400–365 nm) of diazirine molecules.[21,22] Treatment with small-molecule *bis*-diazirine crosslinkers has been shown to enhance fiber strengths, while the development of diazirine-functionalized polyamine primers allowed the introduction of functionality to the aliphatic backbone of the UHMWPE polymer chain (Figure 1).[21] The polymeric primer functions as a bonding layer between the substrate and the adhesive, and the presence of free amine groups on the polymeric layer is the key for switching the character of the substrate from a very low surface energy to a high surface energy material. Topical application of diazirine-based polyamines on polyolefin fabrics is a distinct method that allows easy surface functionalization, not only to improve mechanical strength and to prepare epoxy composites but also to add additional functionality to such challenging polymers. The use of covalent adhesive technology has made it possible to attach dyes or pigments to aliphatic polymeric fibers. In particular, mono-diazirine functionalized dyes have been found to be effective in increasing color yields on polypropylene fabrics.[23,24] However, it should be noted that these dyes require longer fixation

times at high temperatures. Despite this drawback, the covalently linked dye will resist leaching into the environment. This is a significant advantage over conventional disperse dyes (limited to non-polar van der Waals force interactions) that are commonly used for polyolefin fabrics.[25] Poor dyeability is one of the factors that has contributed to a minimal use of polyolefin fabric in the textile and clothing industries.

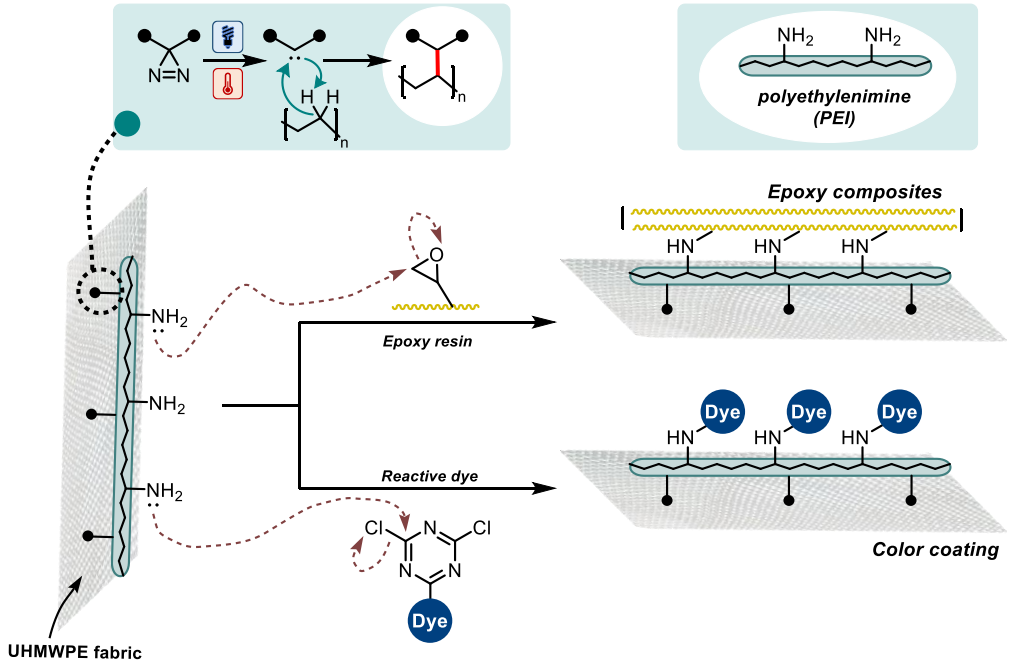



**Figure 1**. Surface functionalization of UHMWPE fabric using diazirine-based polyamine primers.

To tackle the aforementioned concerns and improve the overall performance of the materials, we explored the use of diazirine-based polymers to enhance covalent bonding between primer and substrate and between dyes and UHMWPE fabrics (Figure 1). The presence of diazirine moieties along the branched chains of a polyethylenimine polymer allows the reagents to covalently bond directly to substrate surfaces via C–H, O–H, or N–H insertion while also leading to self-crosslinking, self-aggregation, and irreversible physical entanglement of the primer chains with the substrate chains.

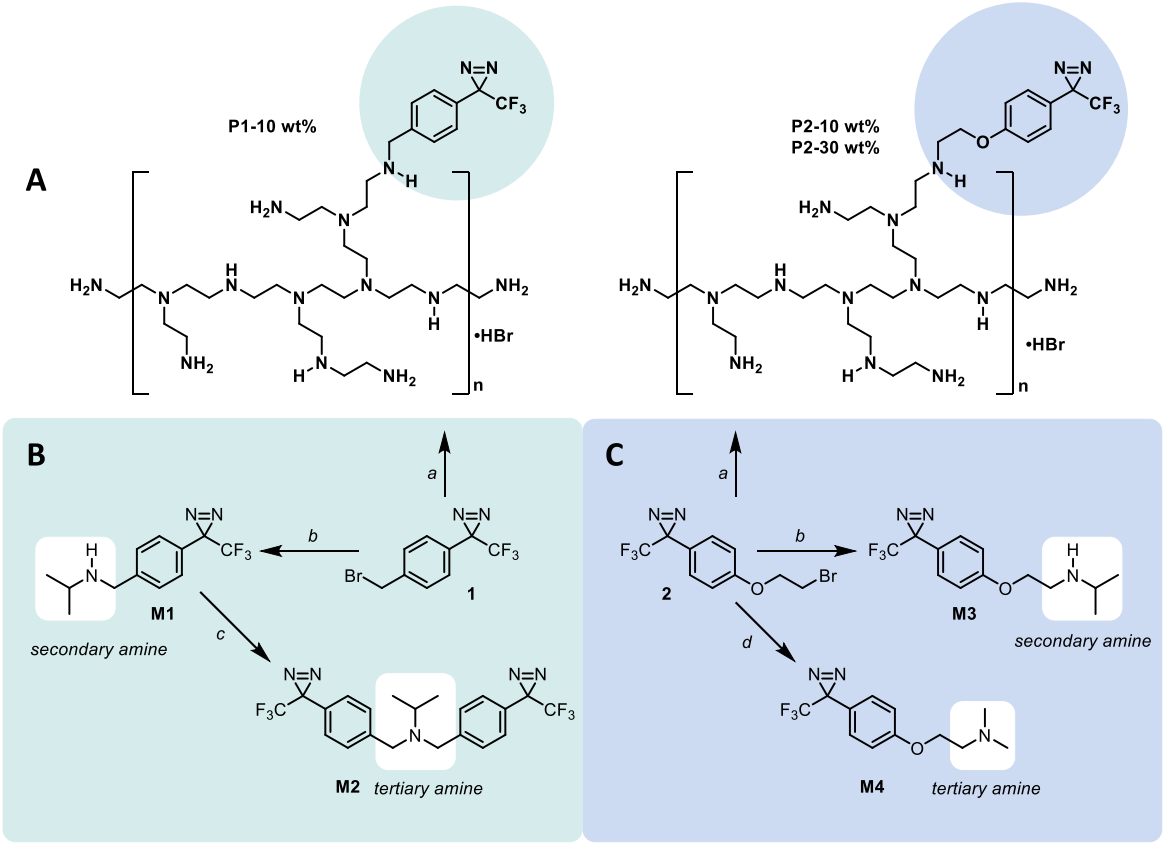
Compared to small molecule-reactive dyes, amine-based primers have the advantage of covalently binding dyes at room temperature in a very short time. Moreover, the coloring depends on the number of amines present on the primed surface, which can react with any commercially available amine-reactive dyes. Importantly, this method allows any commercially available amine-reactive dye to be used and does not require the synthesis of specialty dye conjugates.[23,24] These proprieties overcome the major drawbacks of using small molecule diazirine-based dyes,[23,24] which require high curing temperature for an efficient fixation, and where the color depends on the synthesis of the desired diazirine–dye molecule. Finally, here we show how these molecules can be easily used to encode images or logos on fabric substrates by photocuring the diazirine–polyamine primers using pre-cut masks.

## RESULTS AND DISCUSSION

### 1. Synthesis and Reaction of Primers with UHMWPE Fabric

In this study, we explore the use of two types of polymeric primers: a previously reported electron-neutral diazirine-based polyamine **P1-10 wt%** and two electron-rich variants **P2-10wt%** and **P2-30wt%** shown in Scheme 1. The presence of electron-rich diazirines affords higher C−H insertion yields than in the corresponding electron neutral congener due to a better stabilization of the singlet carbene formation, as previously demonstrated.[20,26] Polymeric diazirine–amine conjugate **P1-10 wt%** was synthesized by reacting branched polyethylenimine (PEI, 25000 g/mol) with 10 wt% of 3-[4-(bromomethyl)phenyl]-3-(trifluoromethyl)-3*H*-diazirine **1**.[21] Meanwhile the electron rich polymeric diazirine **P2** versions were synthesized by addition of either 10 wt% or 30 wt% of 3-(4-(2-bromoethoxy)phenyl)-3-(trifluoromethyl)-3*H*-diazirine **2** to PEI in methanol at 30 °C (Scheme 1) and the expected ratio of diazirine/amine was confirmed by NMR analysis (Table S1). To explore the reactivity of the polymeric primers on the surface of UHMWPE fabric (75

g/m$^2$, 200 denier), the primer **P1-10 wt%**, **P2-10 wt%**, or **P2-30 wt%** was dissolved in methanol at a concentration corresponding to 1 wt% or 5 wt%, relative to the fabric sample that was being treated. The fabric was impregnated for 30 minutes, followed by the evaporation of the solvent. The polymer-impregnated UHMWPE fabric was cured at 110 °C for 4 h in a preheated oven. Gravimetric analysis of the samples was conducted to determine the mass gain after carbene insertion into the fiber chains. After treatment, the fibers underwent three methanolic extractions to remove any byproducts or non-covalently bonded primer. After oven drying the fibers at 100 °C for 5 minutes (to remove residual methanol from the extraction step), the mass retention of each primer was measured.




**Scheme 1**. **(A)** Synthesis of primer **P1-10 wt%**, **P2-10 wt%**, and **P2-30 wt%**; **(B)** electron neutral model compounds **M1** and **M2**; **(C)** electron rich model compounds **M3** and **M4**. Conditions: (a)

MeOH, 0 °C to 30 °C, 48 h; (b) isopropylamine, MeOH, 0 °C to rt, 16 h (**M1:** 91% and **M3:** 88% yield); (c) compound **1**, MeOH, 0 °C to 30 °C, 24 h (**M2**: 83% yield); (d) dimethylamine hydrochloride, $Et_3N$, MeOH, 0 °C to rt, 24 h (**M4:** 81% yield).

In Figure 2A, the amount of primer loaded onto the fabric using thermal curing before methanol extraction is represented by the green bars, and the mass retention after methanol extraction is represented by the blue bars. The vehicle control samples did not add any mass as expected; however, a slight mass loss is reasonably detected due to extensive (3-times) methanolic extraction. Electron-neutral primer **P1-10 wt%** samples retained an average of 74% (5 wt% loading) and 56% (1 wt% loading) of the primer weight after methanol extraction; in contrast, electron-rich primer **P2-10 wt%** samples showed 83% (at 5 wt% loading) and 78% (at 1 wt% loading) of weight retention (Figure 2A), approximately 15% higher than the corresponding **P1-10 wt%**. Increasing the amount of diazirine molecules connected to the polyamine backbone, using primer **P2-30 wt%**, the treated samples retained an average of 84% (at 5wt% loading) and 82% (at 1wt% loading) of primer weight, slightly higher than that for **P2-10 wt%**. Control samples using diazirine-free PEI (at 5 wt% loading) retained 61% of mass after methanol washing (Figure 2A) due to the known thermal decomposition of polyamines during the curing step, which results in insoluble aggregates.[27, 28] Importantly; however, the retained mass in the 5 wt% PEI control samples is less than the retained mass in the samples treated with 5 wt% of **P1** or **P2**, supporting the hypothesis that the diazirine groups are playing a role in binding to the UHMWPE surface.[21]

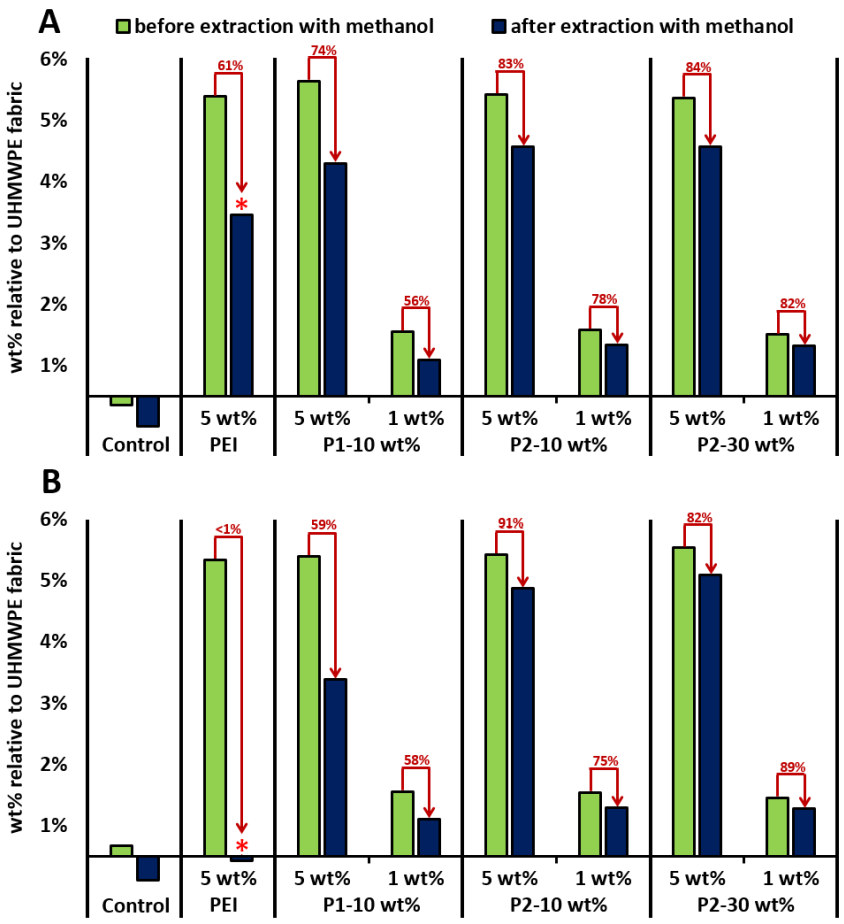



**Figure 2.** Details of 75 g/m$^2$ (200 denier) UHMWPE fabric samples with primer applied **(A)** thermally and **(B)** photochemically (number of replicates=3). Green bars represent the percent of primer before methanolic extraction and blue bars represent the percent of primer retained following methanol extraction. *Retention of mass in the PEI control sample (following thermal activation, but not photochemical activation) is due to the known thermal decomposition of polyamines into insoluble aggregates. Refer to Tables S2 and S3 for raw data associated with each experiment.

Since polyamines are sensitive to thermal decomposition, we replicated the previously discussed gravimetric analysis using a photocuring step to activate the primers. Following photochemical curing, both vehicle control and PEI − contrary to the thermal curing experiment − showed no mass increase after methanol washing (Figure 2B). Electron-neutral primer **P1-10 wt%** showed about 58% weight retention, 24% lower than electron-rich **P2-10 wt%**. On the other hand, electron-rich primer **P2-30 wt%** was retained with an average level of 86%, slightly higher than **P2-10 wt%** (Figure 2B). It is worth mentioning that the thermally cured samples resulted in a discoloration of the UHMWPE fabrics due to amine decomposition. Conversely, photochemically cured samples showed no visible color changes in the fabric, even after prolonged storage (see Figure S8).

To better understand the improved performance of the **P2** primers over **P1** primers and to study the chemical reactivity of **P1** and **P2** on the fabric surface, we carried out insertion experiments using small molecule diazirines containing a terminal amine group as model compounds for **P1** and **P2** and we tested their insertion efficiency. Grafting diazirine molecules onto the PEI backbone will generate a combination of secondary and tertiary amines connected with the aryl diazirine groups. Therefore, for each primer, we designed two types of model compounds: one with a terminal secondary amine and one with a terminal tertiary amine. Electron-neutral **M1** was synthesized by adding isopropylamine to commercially available benzyl bromide **1** (Scheme 1). Subsequent *N*-alkylation of **M1** with another molecule of **1** afforded compound **M2** (Scheme 1). Electron-rich molecule **M3** was synthesized from the corresponding diazirine bromide **2** by adding isopropylamine (Scheme 1). Compound **M4** was separately synthesized from **2** using dimethylamine salt in the presence of triethylamine as a base. To explore the crosslinking efficacy of electron-neutral **M1** and **M2** versus electron rich **M3** and **M4**, C−H insertion experiments were

performed using cyclohexane as a small-molecule surrogate for polyethylene. Upon irradiation with 365 nm for 1 h, **M1** and **M2** afforded 44% and 40% of cyclohexane adducts **C1** and **C2**, whereas **M3** and **M4** yielded 81% and 77% of **C3** and **C4**, respectively (Figure 3A).

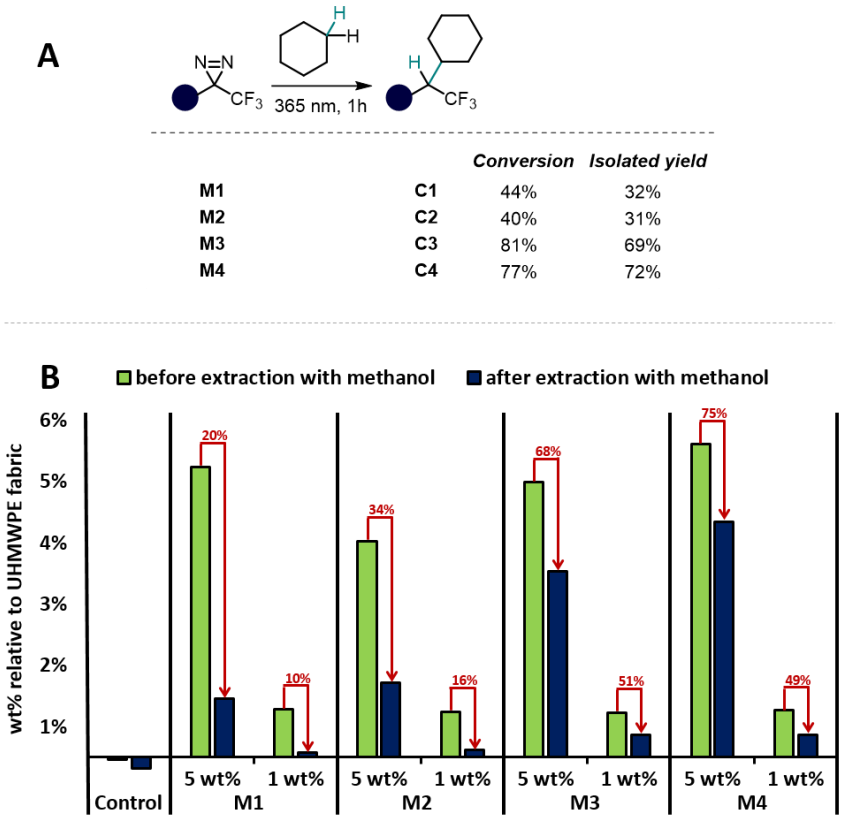



**Figure 3. (A)** Photochemical C–H insertion reactions with cyclohexane, percent conversion of diazirine to **C1-C4** desired adduct and isolated yields measured after column chromatography; **(B)** details of 75 g/m$^2$ (200 denier) UHMWPE fabric samples with model compounds **M1**, **M2**, **M3**, and **M4** applied photochemically (number of replicates=3). Green bars represent the percent of primer before methanolic extraction and blue bars represent the percent of primer retained following methanol extraction. Refer to Table S4 for raw data associated with each experiment.

To test the insertion efficiency of the model molecules on UHMWPE fabric, we photochemically cured 75 g/m$^2$ UHMWPE fabric using **M1**, **M2**, **M3,** and **M4** at loadings of *ca.* 5 wt% and 1 wt% as described above. We found that electron-neutral **M1** and **M2**, which afforded modest yields during the crosslinking experiments in solution, can retain an average of 20% of the mass when applied on UHMWPE fabric after methanolic extraction. The low yields and poor retention for **M1** and **M2** are due to competitive side reactions for the carbene derived from these species caused by triplet carbene insertions (Figure 3 and Table S4). In comparison, electron-rich diazirine **M3-** and **M4**-coated fabric retained more than 60% of the mass added after methanolic extraction, correlating with the higher bonding efficiency obtained using electron-rich carbenes in cyclohexane (Figure 3A). Taken together, these data strongly support the hypothesis that the electron-rich diazirines present in **P2** (and in the small-molecule models **M3** and **M4**) offer superior performance in polyethylene functionalization, relative to the electron-neutral diazirines present in **P1**.

While C–H insertions are desired for functionalization of UHMWPE fabric, competition with N–H bonds present on the backbone of the primer can lead to self-insertion reactions. Carbenes generated from the diazirine units can react non-specifically with any C–H, O–H, or N–H bond in closest proximity. However, carbene reactions are spin-specific, and the reaction pattern depends significantly on the population of equilibrated spin states, which is determined by the free energy singlet-triplet gap and the reaction temperature.[29] To simulate model reactions in solution between the carbene generated from **M1** (electron neutral) and **M3** (electron rich), we conducted insertion experiments in cyclohexane (model for UHMWPE) and isopropanol (backbone model). As previously reported, the presence of electron donating groups attached to a phenyl trifluoromethyl diazirine, as in **M3**, stabilizes the singlet carbene over the triplet in the ground state.[20] Singlet

carbenes react preferentially with the more polar O–H bond in isopropanol through insertion by a concerted mechanism (Scheme S1). By contrast, electron-neutral diazirine **M1** presents triplet and singlet carbenes that are very close in energy, but where the triplet is favored.[20] The high population of triplet carbene leads to preferential C–H insertion products through a hydrogen abstraction/radical recombination pathway. Other side reactions are also possible for triplet carbenes, including undesirable reactions with molecular oxygen to form the corresponding ketone. The preference of **M3** toward O–H insertions suggested that **P2** was likely to engage in a greater number of self-insertion reactions than **P1**, a hypothesis that was subsequently confirmed through solid-state NMR measurements of paraffin and UHMWPE samples treated with **P1-10 wt%** and **P2-10 wt%** (Figures S3–S6). This higher propensity for self-reaction leads to irreversible physical entanglements with substrate polyethylene chains. At the same time, the solid-state NMR data mentioned above also show evidence for C–H insertion from both electron-rich and electron-neutral primers, indicating that both reagents continue to engage in direct covalent functionalization of the polyethylene surface, even as the ratio of C–H to N–H insertion changes with the electronics of the diazirine warhead.

### 2. Reaction of Primer-Treated Fabric with Epoxy Resin

To further investigate the effect of UHMWPE primer-functionalized fabric using both thermally and photochemically activated diazirine polyamines, we treated the surface with epoxy resin and measured the epoxy retention on the fabric. Each sample was prepared by cutting the treated fabrics into three pieces (to permit replicate analysis) of an average size of 1″×5″. Commercially sourced West System Epoxy 105, with no added hardener, was dissolved in methanol, and the treated samples were soaked in the methanolic solution in an aluminum pan; after 30 minutes, the samples were moved onto sheets of aluminum foil and heated at 110 °C for 16 h in preheated oven. The

fabric samples were washed with methanol and dichloromethane three times to remove any unreacted epoxy. As expected, the vehicle control fabrics did not increase mass due to the absence of amine groups in the fabric. On the other hand, primer-coated samples resulted in increased mass due to the successful reaction of the epoxy with the amine-functionalized fabric. As shown in Figure 4A, UHMWPE fabric samples that had been thermally coated with **P1-10 wt%** gained an average of 174% in mass of added resin relative to the initial primer loading. In other words, 1.74 mg of epoxy resin covalently reacted at the surface for every 1 mg of primer that had been added in the initial functionalization step. By contrast, as shown in Figure 4B, fabric samples that had been photochemically coated with **P1-10 wt%** gained an average of 222% in reacted epoxy relative to the initial loading of primer. This increase in efficiency for photochemically vs. thermally primed samples is likely due to the fact that photochemical activation (in contrast to thermal activation) does not trigger the decomposition of the polyamine backbone. This leaves more amine groups free for nucleophilic addition to the electrophilic epoxides present in the added resin. Similar *relative* reactivity with epoxy was observed for UHMWPE fabric samples treated **P2-10 wt%** (173% average increase in mass for thermally primed samples; 201% average increase in mass for photochemically primed samples), but because the **P2** diazirine–polyamine conjugate was more effective at priming the UHMWPE surface in the first step (due to its ability to favor a singlet carbene following diazirine activation) the *total* epoxy loading, relative to the initial mass of the fabric sample, was increased. Thus, a total of nearly 10 wt% epoxy, relative to the mass of UHMWPE, was added following photochemical priming with **P2-10 wt%** and subsequent reaction with epoxy resin. The epoxy loading decreased for primer **P2-30 wt%** since fewer amine groups were available to react with electrophilic epoxide groups present within the resin. Once again, photochemically primed surfaces performed slightly better in reacting with epoxy than did

thermally primed surfaces (120% average increase in mass following thermal activation vs. 128% increase following photochemical activation). As expected, the thermally activated PEI control samples (containing thermally degraded polyamine aggregates on the fabric's surface) gained 1.86 mg for every mg of polyamine material present. In contrast, the photochemically cured PEI control samples contained no measurable PEI amount and were not carried forward to the epoxy treatment step.

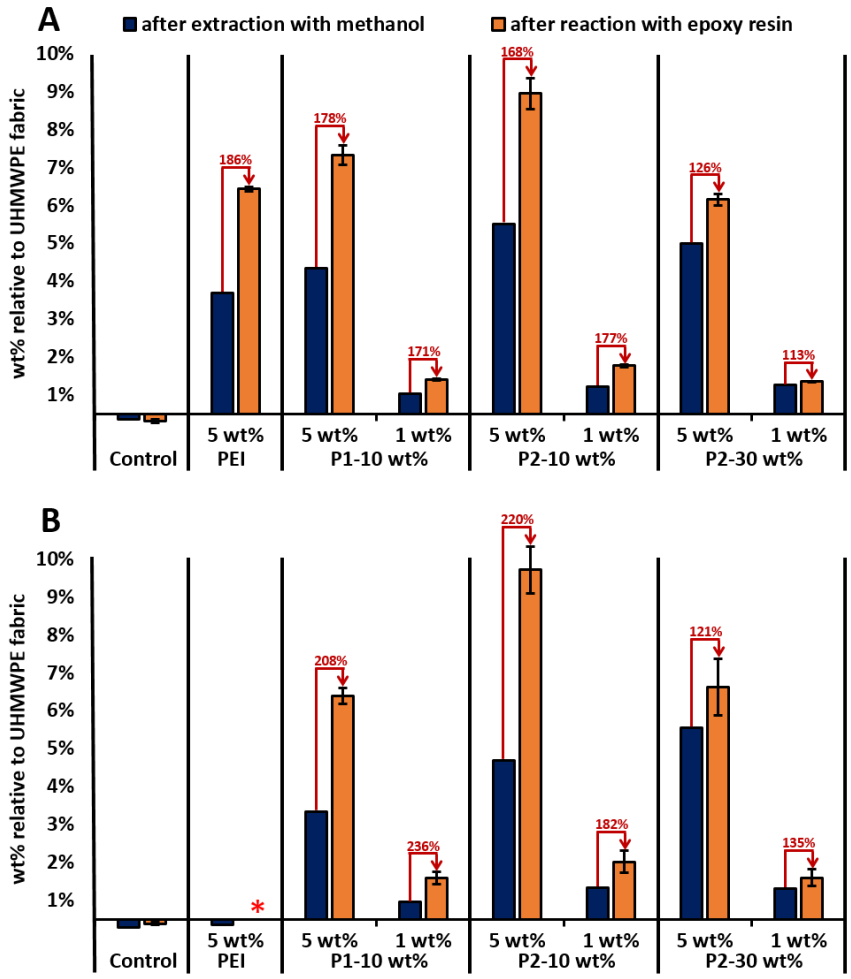



**Figure 4**: Reaction of epoxy resin with polyamine−diazirine primers applied using **(A)** thermal activation and **(B)** photochemical activation. Numbers in red indicate the weight percent of reacted epoxy relative to the mass of the loaded primer reagent. Error bars indicate standard error over

three replicates. *The sample contained no measurable PEI amount and was not carried forward to the epoxy treatment step. Refer to Tables S7 and S8 for numbers of replicates used for each test condition, and for the raw data associated with each experiment.

### 3. Surface Characterization

We conducted a series of water contact angle measurements to gain further insight into the modified polymer surface resulting from primer activation using different methods. We compared the untreated UHWMPE fabric to the samples treated with various primers cured thermally and photochemically, and measured the contact angles of the samples treated before and after addition of epoxy resin. We found differences in the contact angle depending on the activation method. For example, thermally cured samples with primer **P1** and **P2** exhibited a contact angle of around 100°, slightly lower than that of the vehicle control (116°; Table S9 and Figure S2A). Furthermore, adding epoxy resin did not significantly change the contact angle (Figure S2B).

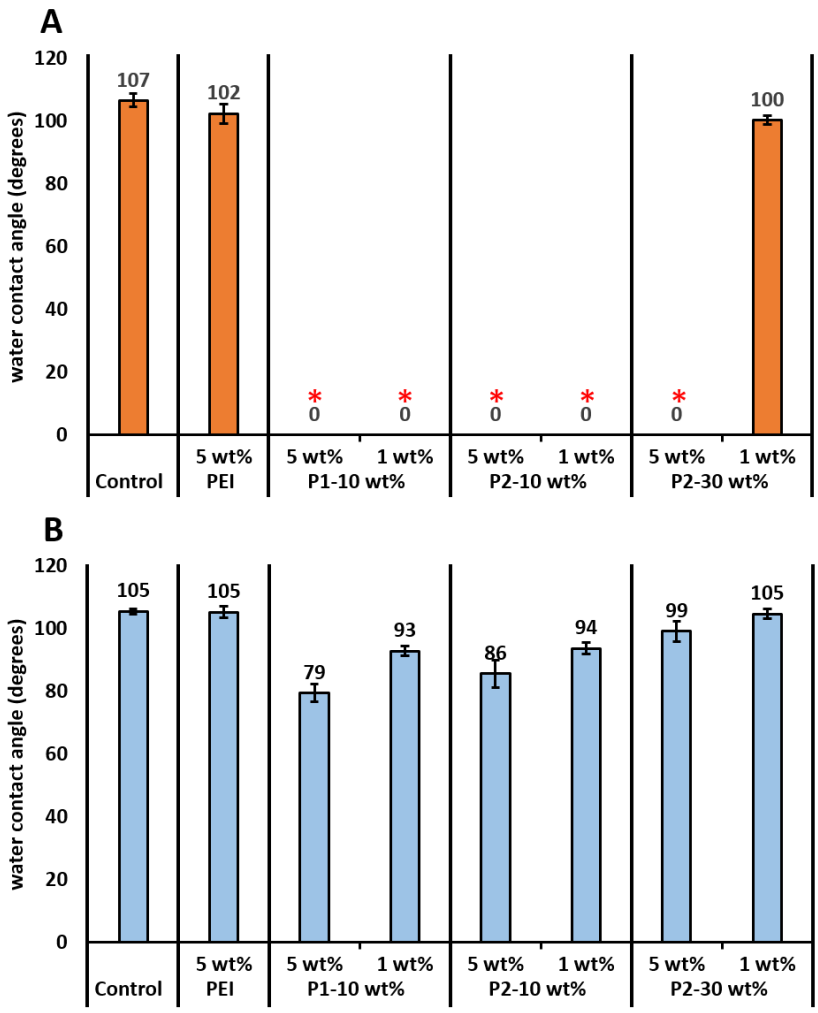



**Figure 5. (A)** The average water contact angle of UHMWPE surfaces to which polyamine−diazirine primers were applied photochemically **(B)** Average water contact angle of photochemically applied primer-coated surfaces reacted with epoxy resin. *Asterisks indicate that a zero-degree contact angle was recorded. Error bars indicate standard error over 5 replicates. Refer to table S9 for the raw data associated with each experiment.

In contrast, the photochemically cured samples dramatically increased the hydrophilicity of the polymeric fiber; for example, the water droplets were immediately absorbed in the fabric coated

with 5 wt% of **P1-10 wt%**, **P2-30 wt%** and **P2-10 wt%**. (Figure 5A). However, when the fabric was coated with only 1wt% of **P1-10 wt%** or **P2-10 wt%**, the water droplets took *ca.* 200 seconds to soak entirely into the fabric. In comparison, the vehicle control fabric did not absorb the water droplet during the first 20 minutes; the experiments were stopped after that time. Dissimilarly, samples treated with 1 wt% of primer **P2-30 wt%** only somewhat reduced surface hydrophobicity compared to the vehicle control, and an average contact angle of 100° was observed. This result makes sense in light of the different availability of primary amine groups present in **P2-10 wt%** compared with **P2-30 wt%**. In the latter reagent, a larger percentage of amines have been reacted with electrophilic diazirine groups, rendering them less able to contribute to increasing the surface energy of the sample. Additionally, the greater number of diazirines present within the primer means that a larger number of N–H bonds will undergo insertion reactions in the photocuring step, further limiting their ability to increase the hydrophilicity of the fabric surface. This dual effect makes **P2-30 wt%** somewhat less effective at increasing the UHMWPE's surface energy when a low loading of primer is used. When a higher loading is employed, however, the surface is still rendered hydrophilic.

### 4. Dyeing of Primer-Treated UHMWPE Fabric

Surface modification of UHMWPE fabrics using amine primers improves surface polarity and reactivity. Previous reports showed how polyethyleneimine immobilized into cellulose using carbamate linkages helps to improve the dyeing properties of the fiber through an absorption mechanism involving an electrostatic ion-dipole attraction between the protonated amines of PEI and the negatively charged groups of the dye.[30] Similarly, the active functional layer of amines can quickly react with amine-reactive dyes, forming covalent linkages on the fabric. To verify the dyeing capability of the primed fabrics, we selected photochemically cured samples as they offer

a much cleaner surface compared to thermally cured material, and we treated them with a commercially available dye that contained a cyanurate motif capable of covalently modifying amines. In a beaker, Reactive Blue 4 was dissolved in methanol; photochemically coated fabric samples (using **P1** and **P2**) were dipped in the dye solution for 5 minutes at room temperature. Each sample was washed three times with methanol at room temperature to remove the unreacted dye not attached to the fabric. A vehicle control sample (without primer) and PEI treated sample were also soaked in the dye solution following the same procedure. The color durability of dyed fabrics with Reactive Blue 4 was evaluated by the AATCC Test Method 124 standard protocol reported in the literature.[31] As shown in Figure 6A, the strong covalent linkage between the amine-primed surface and reactive dye on the fabric surface retains the color shade before and after washing the fabrics. Additionally, to explore the photopatterning of the dye color onto the fabric surface, we investigated using **P1** and **P2** for textile printing. The printing process involves the addition of the dye to specific areas of the fabric. By simply applying a pre-cut mask (in this case, we used the University of Victoria logo – UVIC) on the UHMWPE fabric coated with **P2-10 wt%** during the photocuring step, and then adding the desired dye, the UVIC logo appeared with high definition on the surface as shown in Figure 6B. Since we observed fabric discoloration using thermal curing, we used the effect of the thermal decomposition of amines to display the logo printing without adding extra dye. After photochemically curing the primer using the mask, the fabric was kept in the oven at 100 °C for 4 hours. As a result, a solid yellow-colored UVIC logo appeared on the UHMWPE fabric, as shown in Figure 6C. The high quality logo printing into the fabric offers the potential of polyamine-coated-UHMWPE fabric for precise dyeing applications and many other coating functionalizations with amine-reactive reagents.

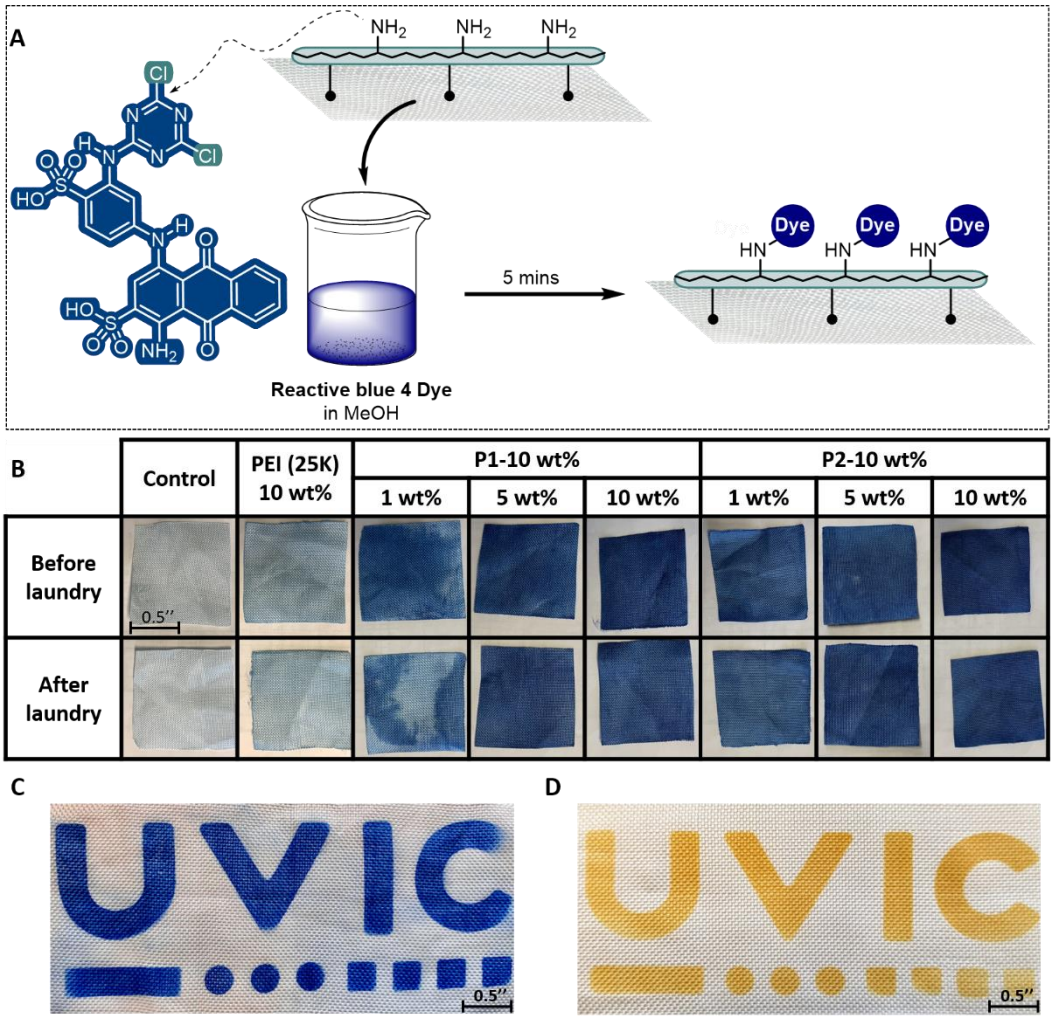



**Figure 6. (A)** Treatment of amine-primed surface with reactive dye; **(B)** photographs of colored UV crosslinked UHMWPE fabric samples after dye reaction before laundry washing with methanol and after laundry cycle using the AATCC 124 standard protocol; **(C)** UVIC logo printing using Reactive Blue 4: each letter is photochemically primed using **P2-10 wt%** at 5 wt% loading under UV for 30 seconds using a pre-cut mask, and followed by the reaction with dye; **(D)** UVIC logo printing through intentional decomposition of covalently linked primer: each letter is photochemically primed using **P2-10 wt%** at 5 wt% loading under UV for 30 seconds using a pre-cut mask, followed by oven heating at 100 °C for 4 hours. For an accompanying gravimetric analysis following curing, dyeing, and washing, refer to Figure S10.

## CONCLUSION

In summary, we designed and synthesized two electronically optimized diazirine-containing primers (**P2-10 wt%** and **P2-30 wt%**) and compared them with a previously synthesized electron-neutral diazirine-based polyamine **P1-10 wt%**. The obtained data indicate that electron-neutral and electron-rich polyamine–diazirine primers were successfully grafted onto UHMWPE fibers; however, the electron-rich primers resulted in higher retention and efficiency in comparison with the **P1** primer. This covalent adhesion was also supported by the fabric's further functionalization using an epoxy resin followed by extensive washing steps. Moreover, efficient surface functionalization was shown using an amine-reactive dye that covalently bonded to the fabric with extremely high color fastness. The color durability of dyed fabrics with Reactive Blue 4 was evaluated using the AATCC 124 standard protocol. Introducing a pre-cut mask to block the light from reaching specific areas of the fabric material during the photocuring step of the diazirine-containing primer allows for the facile encoding of images or logos into the weaves.

Challenges in the functionalization of UHMWPE fabrics can be overcome by the topical application of **P2** or **P1** primers under mild reaction conditions. Diazirine primers function through a distinct mechanism of action from traditional surface modification approaches, without introducing further challenges in the application and curing steps and without destructively modifying the fabric. As little as 30 seconds is needed to photochemically activate diazirine-containing primers and generate strong covalent bonds with low-surface-energy materials such as polyethylene.

ASSOCIATED CONTENT

Supporting figures and tables, complete experimental details, numerical data used to create the plots, relevant $^{1}H$ and $^{13}C$ spectra.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Funding Sources

Innovate BC: grant 184-RND8-2019.

## Notes

The authors declare the following competing financial interest(s): Authors Nazir, Musolino, and Wulff are co-inventors on patent applications PCT/CA2022/050293 and PCT/CA2022/051500, which claim the use of primers described in the current manuscript.

ACKNOWLEDGMENT

The authors gratefully acknowledge funding from Innovate BC (grant 184-RND8-2019). R.N. and S.F.M. additionally thank Mitacs Canada (grants IT11982 and IT17318) for fellowships, and XLYNX Materials for operating funds that were used to support this research. The authors thank the staff at the Advanced Microscopy Facility at the University of Victoria for assistance with the SEM measurements, and Dr. Eric Ye at the Simon Fraser University NMR Facility for collecting the solid state $^{19}F$ NMR data. We also thank Prof. Alexandre Brolo for co-supervision of R.N., and for operational assistance during the completion of this project.

ABBREVIATIONS

PEI, polyethylenimine; UHMWPE, ultra-high-molecular weight polyethylene.

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