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Design of flameproof and waterproof natural textile fabrics

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ABSTRACT

Natural fabrics, particularly linen and cotton are widely used in the textile industry due to their desirable properties, including breathability, durability, and comfort. However, their hydrophilic nature and inherent flammability pose limitations on their applications in various areas, such as residential settings, automotive vehicles, offices, and protective clothing. In these contexts, flame-retardant and hydrophobic properties are of crucial importance. To address this issue, we have applied UV-curable coatings on the surface of linen and cotton fabrics by employing two distinct acrylic polymer synthesis strategies. In the first approach, a methacrylated phenolic lipid was combined with n-alkyl methacrylate and copolymerized under UV exposure resulting in a hydrophobic and flame-retardant surface. In the second approach, 3-Aminopropyltriethoxysilane is coated on the natural fabric, and then 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is applied above the 3-Aminopropyltriethoxysilane (APTES) surface prior to UV curing. A comprehensive study was conducted to evaluate the wetting behavior and flame retardancy of the fabric both before and after coating. This was done by employing water contact angle and limiting oxygen index testing. The findings of this study demonstrate that the hydrophobicity and flame retardancy of the fabric can be substantially enhanced through UV coating. Furthermore, the initial ratio between the applied monomers can be adjusted to fine-tune these properties. It is noteworthy that all the chemicals utilized in these investigations are derived from renewable bioresources, thereby ensuring sustainability and biocompatibility. This aspect holds significant importance for the textile industry, aligning with the growing demand for environmentally friendly and socially responsible manufacturing practices.

I. INTRODUCTION

The global textile fabrics market, valued at $920 billion in 2018, is projected to expand to $942.8 billion by 2024, with a projected compound annual growth rate (CAGR) of 5% [1]. Natural textiles, particularly cotton and linen are cornerstones of the textile industry, offering a myriad of features. For instance, cotton is the most significant natural fiber used in textiles, accounting for approximately 38% of the total fiber market in 2023 [2]. It is a popular choice for clothing and home textiles because it absorbs moisture well, is breathable, and is comfortable to wear. Linen, which comes from the flax plant, is another important natural textile fiber. Compared to cotton, linen is about 2-3 times stronger [3]. However, hydrophilic nature and flammability of these natural textiles present significant challenges that limit their potential applications [3,4]. These limitations have spurred efforts to develop treatments and finishes that enhance properties of natural textiles, including water repellency and flame retardancy, thereby broadening their application range [5,6]. However, it is crucial to consider the environmental and health implications of such treatments [7,8].

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Photocurable coatings offer a state-of-the-art method for enhancing the properties of natural fabrics, particularly in the areas of flame retardancy and water repellency [8]. Characterized by rapid, low-temperature curing and solvent-free composition, this technology not only saves energy, but also reduces environmental impact by eliminating volatile organic compounds [9,10]. Its versatility and cost-effectiveness make it a top choice for industries seeking efficient, high-performance coating solutions for a wide range of substrates. On the other hand, the increasing adoption of bio-based materials in coating applications is driven by their environmental sustainability and superior performance attributes. Derived from renewable resources, they reduce reliance on finite fossil fuels and exhibit low volatile organic compound emissions, promoting both environmental and human [11,12]. Additionally, their biodegradability and enhanced performance characteristics, such as superior barrier properties and durability, make them an appealing choice for industries seeking environmentally sustainable and high-performance coating solutions [13].

Despite the advantages that biobased acrylates present for photocurable textile coatings, research in this area is still in its infancy. Only a limited number of studies have specifically addressed the potential use of these acrylics in textiles. In a related study, Wu et al. [14] investigated the potential of bio-based furanic di(meth)acrylates as reactive diluents for UV-curable coatings. They highlighted the renewable nature of these materials and suggested that they could possess unique properties that could improve textile coating performance. However, these materials remain understudied regarding their use in textile-specific applications, thus creating a need for further research into their potential for enhanced functionality. Similarly, Seker et al. [15] investigated fully bio-based thiol-ene photocured thermosets, providing insights into alternative systems that could potentially replace or complement traditional acrylate-based coatings. The findings indicated that these biobased coatings demonstrated comparable performance to that of petroleum-based coatings; however, research specific to textile applications remains limited. Lin et al. [16] underscored the importance of understanding the stability and interactions between biobased acrylates and substrates. However, their work primarily focused on general coating applications, thereby underscoring the need for textile-centered studies. In a recent study, Liu et al. [17] demonstrated the effectiveness of acrylated soybean oil as a monomer for photocurable coatings. They noted the ability of this monomer to undergo photopolymerization, producing coatings with desirable mechanical properties. Nevertheless, the study does not address the broader range of biobased acrylates with multifunctionality, such as water-repellant and flame-retardant properties that could be further investigated for their potential use in photocurable applications.

In this study, an effort was undertaken to enhance the properties of natural fabrics including linen and cotton by applying photocurable coatings derived from bio-based renewable materials. This endeavor involved two distinct strategies for synthesizing photosensitive polymers. In the first method, methacrylated phenolic lipid was combined with n-alkyl methacrylate, initiating copolymerization under UV exposure. This process yielded a surface that was not only hydrophobic but also exhibited flame-retardant properties. In the second approach, the fabric was coated with 3-aminopropyltriethoxysilane, followed by the application of acrylated 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide before UV curing. Subsequently, a comprehensive evaluation of the fabric's wetting behavior and flame retardancy was conducted, both pre- and post-coating, utilizing water contact angle (WCA) and Limiting Oxygen Index Testing (LOI).

II. EXPERIMENTAL METHOD

2.1 Materials

Linen (Color: light yellow, purity:100%, Pattern: Closely-Woven, weight per unit area: 122 g/m^2) and cotton (Color: grey, purity:100%, pattern: Pile Weave, weight per unit area: 179 g/m^2) fabrics were purchased from Bursa fabric market. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from MCT CHEM, while Cardanol NX 2026 was sourced from Cardolite Corporation, India. BASF supplied various alkyl-acrylates (C12 and C18), and 1-Hydroxycyclohexylphenyl ketone (Irgacure 184) was purchased from Ciba Specialty Chemicals. Glycidyl methacrylate (GMA) (99% min), triethylamine (TEA), and hydroquinone (HQ) were procured from ATAMAN KIMYA, Türkiye. Hydrogen peroxide was obtained from Tekkim Kimya, while 3-(Aminopropyl)triethoxysilane (APTES) was sourced from Wacker Chemie. Dimethylbenzyl amine and n-hexane were acquired from Sigma Aldrich.

2.2 Synthesis of photo-sensitive acrylics

2.2.1. Modification of Cardanol with GMA (CGM)

Cardanol was modified with GMA according to previously applied procedure [18]. TEA as catalyst and hydroquinone as inhibitor were added to a mixture of cardanol and GMA in a molar ratio of 1:1 in a flask and the reaction was stirred at 60-70 °C for 5-6 hours. After cooling, the product was diluted with ethyl acetate and was washed with a solution of NaOH to remove unreacted components.

2.2.2. Modification of DOPO with GMA (DOPO-GMA)

DOPO reacted with ethanol and hydrogen peroxide, followed by recrystallization and drying to yield a white solid (DOPO-OH) [19]. The DOPO adduct was then reacted with glycidyl methacrylate in presence of N,N-dimethylbenzyl amine as catalyst in tetrahydrofuran solvent to produce DOPO-glycidyl methacrylate (DOPO-GMA).

2.3 Performing coating via UV curing

In the first approach, the synthesized CGM was prepared by mixing different ratios of C12/C18 monomers in acrylic monomer. The fabric surfaces of linen and cotton were dipped by adding with Irgacure 184 (PI) and TMPTA (CL) to the mixture. After filtering, the fabrics were cured in the UV cabinet for 30 minutes.

In the second approach, the fabric surface was first modified with APTES, then the synthesized DOPO-GMA was mixed with irgacure 184 (3%) and TMPTA (2%) was applied on top of the APTES before UV curing for 30 minutes. The list of the coating samples is shown in the table below:

Table 1. The composition of prepared resin for UV curable resin

Resin	CGM	C12	C18	DOPO-GMA	PI	CL
A	95	-	-	-	3	2
B	55	40	-	-	3	2
C	35	60	-	-	3	2
D	15	80	-	-	3	2
E	60	17.5	17.5	-	3	2
F	-	-	-	95	3	2

2.4 Characterization

The synthesis of photocurable chemicals were confirmed via One-Hertz nuclear magnetic resonance (^{1}H NMR) spectra obtained by an Agilent VNMRS spectrometer operating at 500 MHz spectra with dichloromethane ($CDCl_3$) serving as the solvent. The modification of DOPO was traced by FTIR test, with spectra obtained in the region 4000–700 cm^{-1} using a JASCO FT/IR-4200 spectrometer, at a resolution of 4 cm^{-1} with 16 scans. The hydrophobic properties of prepared coatings were determined by WCA measured in a Biolin Scientific Attension Theta Lite Model Optical Tensiometer. The flame retardancy of the chemicals were determined by the LOI values of the prepared films in the size of 50 × 10 × 1 mm^3 using a LOI (Devotrans) type instrument, in accordance with ASTM D2863-08 standards.

III. RESULTS AND DISCUSSIONS

3.1 CGM-based photocurable coating

Figure 1 shows the ^{1}H NMR of CGM where the hydroxyl proton can be observed at a shift of 3.29 ppm. When we examined the ^{1}H NMR peaks, the peak at 6.9 ppm indicated the protons of phenolic structure. Due to the ring activating feature of the cardanol substituting group, the b protons appear at a higher level at 6.6 ppm. c, d, e in the range of 6-4.7.5 ppm indicated double bond protons.

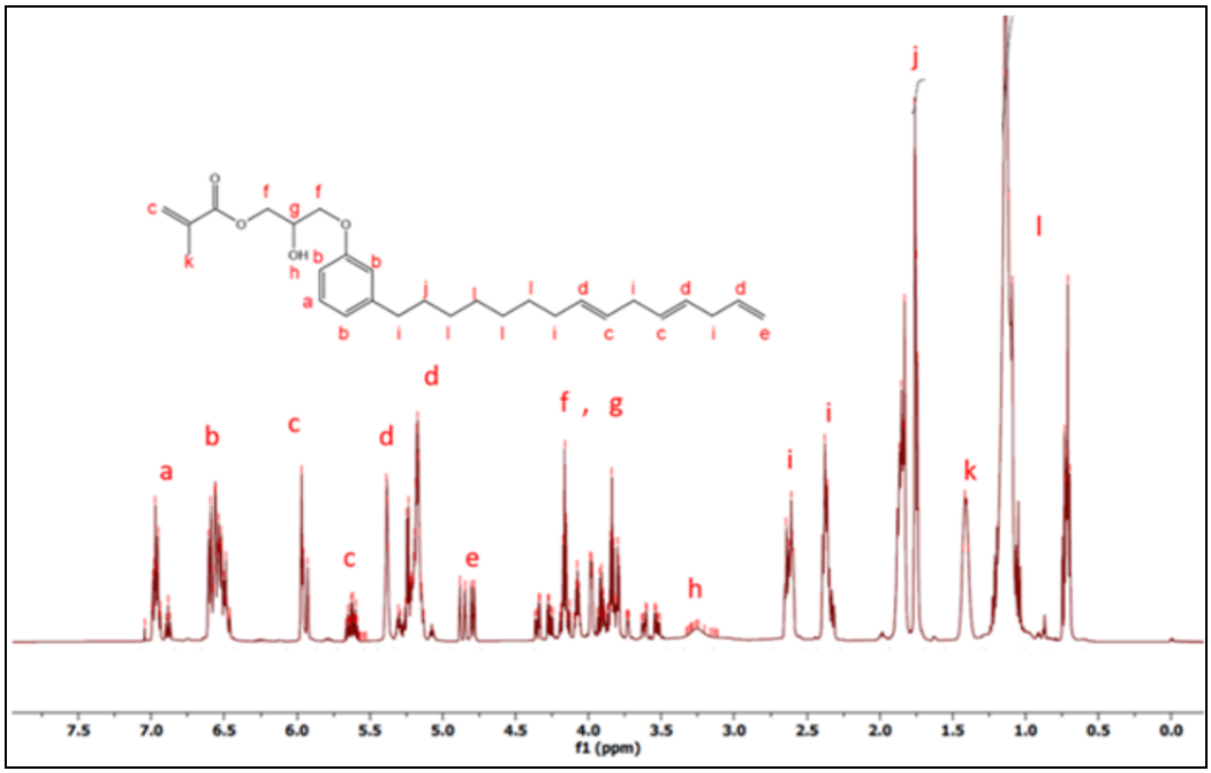

Figure 1. ^{1}H NMR result of CGM monomer

The acrylation of DOPO is evidenced by Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) as shown in Figure 2. Typical peaks observed at 1242 cm^{-1} (P=O) and 910 cm^{-1} (P-O-phenyl) are characteristic of DOPO. The peaks within the 1580–1610 cm^{-1} range originate from the aromatic rings inherent in

the DOPO structure. Moreover, in DOPO-GMA, an absorption band emerges near 1650 cm^{-1}, indicative of the stretching vibration of the vinyl C=C bond, a hallmark of acrylated chemical structures.

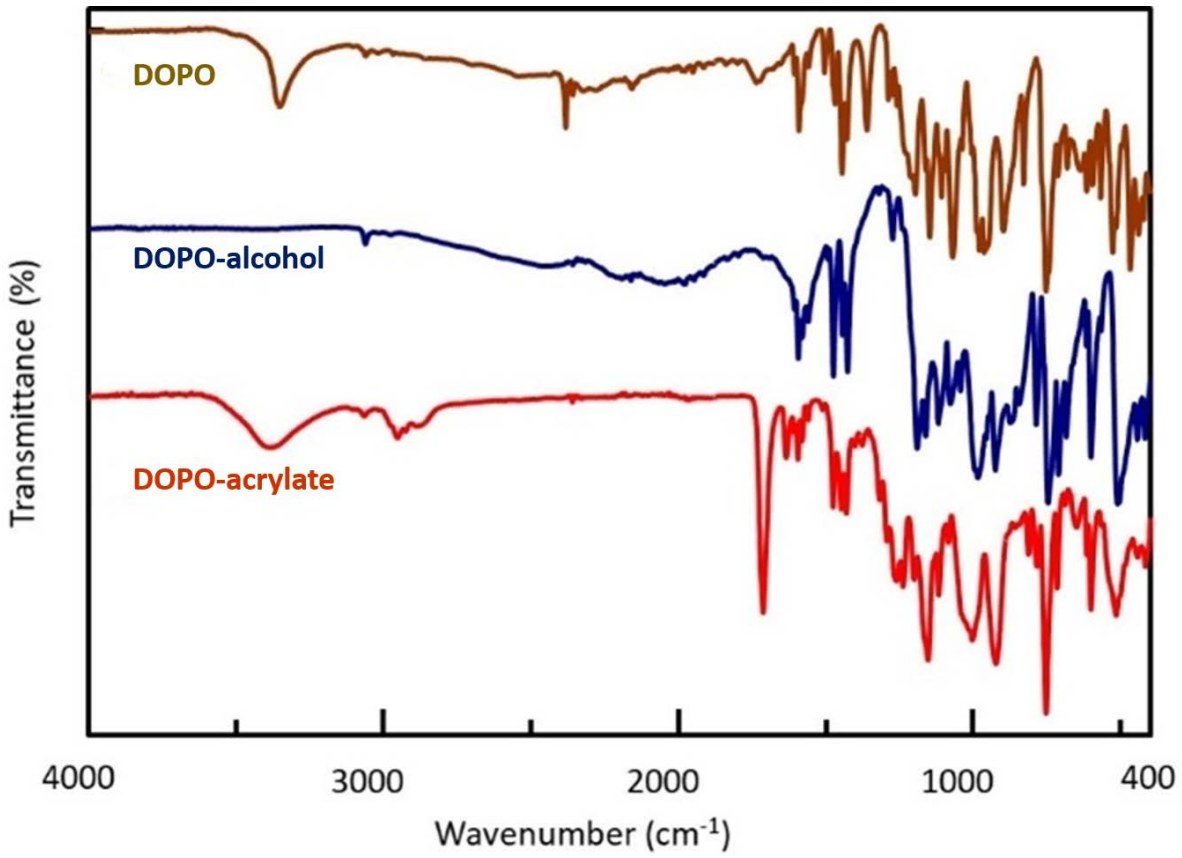

Figure 2. FTIR spectra showing the acrylation reaction of DOPO

Figure 3 illustrates the WCA of linen and cotton prior to and following the application of a variety of compositions derived from UV-curable resins. Pure linen exhibited a WCA of 38°, with the addition of CSM having only a modest effect on enhancing the hydrophobicity of linen. While cardanol possesses certain hydrophobic properties due to its long alkyl chain, it also contains polar groups, such as the hydroxyl group (-OH), which contribute to its overall hydrophilic nature. The incorporation of alkyl acrylate (C12/C18), particularly longer ones, into CSM enhances hydrophobicity by introducing a long hydrophobic alkyl chain. For instance, the addition of 17.5% C18 resulted in a WCA of 98.5°. This is because the hydrophobic alkyl chain reduces the affinity of the material for water molecules, making it more water-repellent. The steric hindrance created by the bulky alkyl chain further prevents water molecules from interacting with the material's surface. Additionally, the methacrylate groups in C12/C18 allow for copolymerization with cardanol, resulting in tailored copolymers with improved hydrophobicity. The results also demonstrate that the hydrophilicity of linen can be markedly enhanced by coating with DOPO-GMA, due to the presence of nonpolar hydrocarbon groups in its structure, which impede the interaction between water molecules and the material's surface. The trend of an increase in WCA for cotton after coating was found to be analogous to the observed phenomenon for linen. Nevertheless, the WCA for cotton remained inferior to that of linen due to intrinsic fibre differences. The smoother surface and higher hydrophilicity of cotton permit greater water absorption, whereas the rougher texture and higher lignin content of linen trap air,

thereby promoting hydrophobicity [20]. The effectiveness of the coating is also contingent upon its interaction with said fiber that the coarser structure of linen may provide superior adhesion and hydrophobic enhancement than cotton, which is in alignment with the findings regarding surface chemistry and coating compatibility.

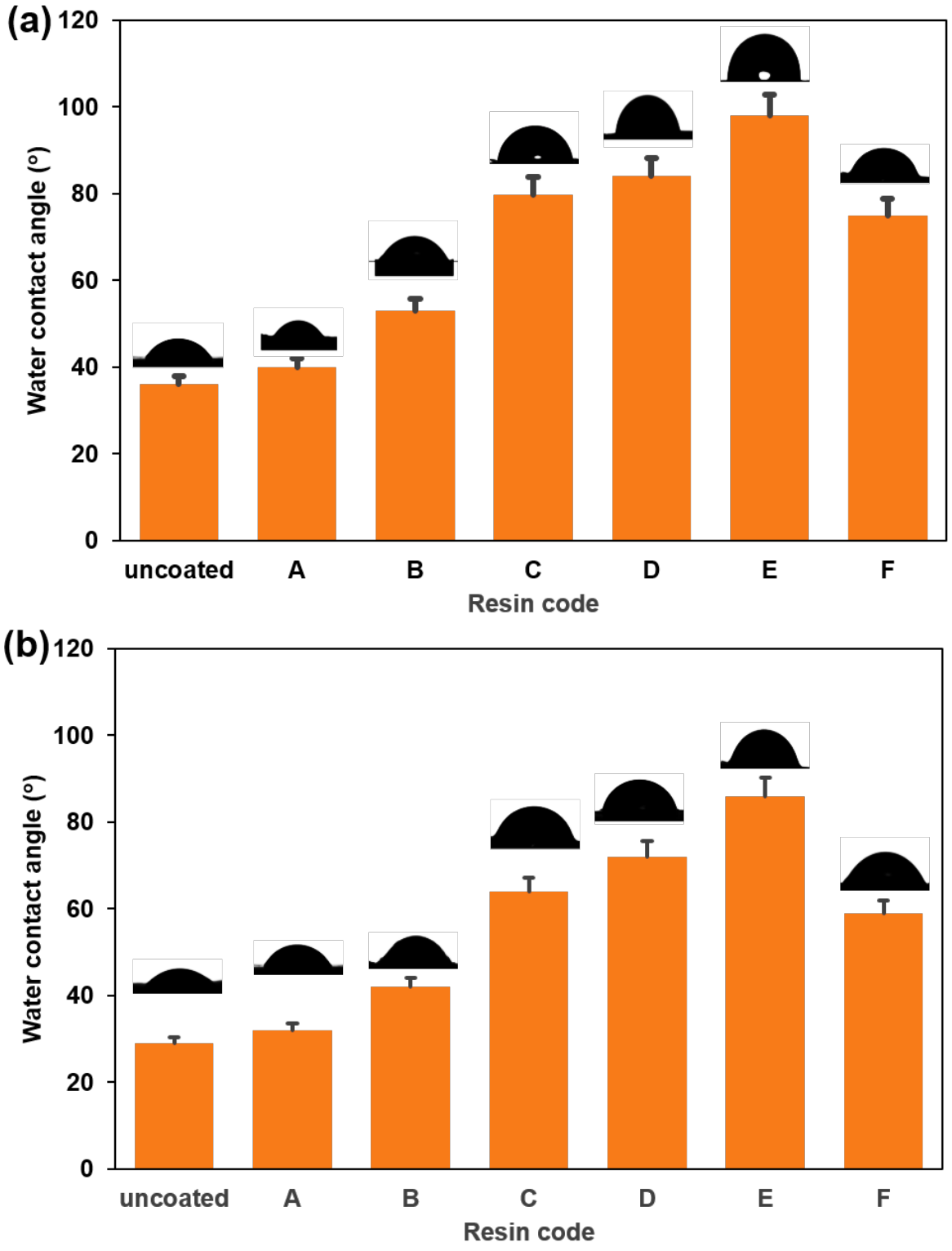

Figure 3. WCA of linen (a) and (b) cotton before (noted as uncoated) and after coating with UV-curable resins

As demonstrated in Table 2, the LOI values of textiles prior to and following the application of UV-curable resins highlight the influence of varying resin formulations on flame resistance. The combination of alkyl acrylate and CSM resulted in a modest increase in LOI, whereas a more pronounced enhancement was observed with DOPO-GMA (Resin F). In particular, the LOI values of linen and cotton fabrics coated with the DOPO-acrylate mixture increased to 25.9% and 24.4%, respectively, in comparison to their baseline values of approximately 18%. This notable enhancement illustrates the efficacy of DOPO-based formulations in augmenting the flame-retardant attributes of natural fabrics, rendering them safer for applications where fire resistance is paramount. DOPO is a widely used flame retardant that has been demonstrated to reduce the flammability of materials through the interference of combustion reactions and the formation of a protective char layer. This layer acts to delay or inhibit the spread of flames, making it a highly preferred additive in the textile industry for enhancing fire safety.

Table 2. LOI of linen (a) and (b) cotton before (noted as uncoated) and after coating with UV-curable resins

Textile type	Linen LOI value (%)	Cotton LOI value (%)
Uncoated	18.0	18.4
A	18.0	18.2
B	19.0	18.7
C	19.6	19.0
D	20.2	19.7
E	20.0	20.6
F	25.9	24.4

IV. CONCLUSIONS

In conclusion, the water repellency and flame retardancy of linen and cotton were enhanced through the application of photocurable coatings utilizing newly developed resins derived from bio-based renewable materials. The results of this study demonstrate notable progress in the development of multifunctional protective coatings for natural fabrics via UV-curing systems. The combination of methacrylated phenolic lipids, n-alkyl methacrylate, and DOPO represent a novel approach to the development of protective fabric treatments. The WCA of 98.5° was achieved by means of the synergistic effect of alkyl acrylate and CSM, which aligns with previous studies by Jain et al. [21] and Bhuiyan et al.[22]. In their studies, the WCA ranged from 88° to 101° and was obtained using different hydrophobic coating systems. However, our method offers the advantage of a simpler, one-step UV curing process in comparison to the multi-step approaches described in previous studies.

The modification of DOPO with glycidyl methacrylate (resin F) followed by UV curing produced notably favourable outcomes with respect to flame retardancy, with LOI values increasing to 25.9% for linen and 24.4% for cotton, in comparison to the untreated fabrics with LOI values of approximately 18%. These findings are comparable to the work of An et al. [23], who previously developed textile fabrics with flame retardancy by depositing graphene, casein, and ammonium polyphosphate on their surface via layer-by-layer assembly. The UV-cured DOPO-GM system exhibited comparable flame-retardant properties while markedly reducing processing time and energy consumption. The vertical flame test results demonstrated enhanced char formation and a reduction in post-ignition glow time in comparison to the phosphorus-based flame retardants documented in the literature.

In conclusion, this new approach to fabric treatment represents a significant step forward in the development of more efficient and effective protective coating systems. By combining hydrophobicity and flame retardancy in a single coating, it addresses a major gap in the current literature on protective fabric treatment. However, further optimization and durability studies are needed to fully realize the potential of this new system for commercial applications. Firstly, a systematic investigation is required in order to determine the optimal parameters for UV curing, specifically in terms of exposure time, intensity, and photoinitiator concentration. This will enable the coating performance to be maximized. Secondly, the potential for synergistic effects between different acrylate compounds must be investigated in order to further enhance both hydrophobicity and flame retardancy. Previous studies have primarily focused on optimizing either property independently, thus making our proposed combined approach a novel contribution to the field. Moreover, although the preliminary results indicate encouraging durability, long-term stability studies under diverse environmental conditions are essential to substantiate the practical viability of the coating. Future work will also examine the scalability of this coating system for industrial applications, as current UV-curing methods in textile finishing frequently encounter difficulties in maintaining uniform coverage over extensive surface areas.

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