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Mechanical Performance of Protective Epoxy Coatings with Bio-Based Ingredients for Flax–Fiber Composites †

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Abstract: Due to its long and continuous cellulose fibers, flax offers excellent specific tensile strength and stiffness relative to other natural fibers such sisal or jute, and it is widely used as fiber reinforcement in composites with relevance in industries such as automotive, sports and maritime environments. However, the use of natural fibers poses additional challenges relative to synthetic fibers in ensuring the functional lifetime of composites; in particular, water resistance and resistance against UV conditions should be improved for outdoor use. Therefore, a protective coating that offers high resistance against environmental conditions and mechanical damage can be applied to avoid direct surface exposure of natural fibers. The linseed oil or wax coatings increase the hydrophobic surface properties and limit water ingress, but they have drawbacks such as extended curing periods via oxidative crosslinking and weak mechanical performance. In seeking alternatives for natural fiber composites, the potential of bio-based crosslinked coatings to enhance mechanical robustness, surface protection and durability was explored by screening various coating grades, including bio-based epoxy resin, diluents and crosslinkers. The epoxy coatings with a bio-based phenalkamine crosslinker offer higher hardness and scratch resistance, and the water resistance was improved in the presence of an amine crosslinker with long alkyl chains. In parallel, the mechanical abrasion resistance of the crosslinked coatings significantly increased in relation to the intrinsic mechanical properties and crosslinking density of the coatings. The processing of the epoxy coatings was further enhanced by adding a bio-based trifunctional diluent with low viscosity while providing limited shrinkage and good compatibility with the composite substrate. Moreover, the UV resistance was better for epoxy coatings with a bio-based diluent, likely via migration effects and the formation of a protective layer at the outer surface.

Keywords: composites; lifetime; protection; coating; water resistance; mechanical resistance

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1. Introduction

Natural fiber composites can offer a sustainable replacement for common composite materials, where naturally sourced fibers from annual plants or agricultural residues may replace traditional reinforcement fibers such as glass or carbon fibers. Typical composite applications are products that require high structural efficiency and long-time reliability, e.g., those used in the aerospace, energy, construction and sports industries. The fibers determine the material strength and stiffness, and the polymer matrix dominates the surface properties such as roughness and outdoor resistance. The production of glass and carbon fiber is very energy-intensive; in addition, it is a challenge for traditional composites to preserve the material value during the end-of-life [1]. Alternatively, the long flax fibers that are specifically grown and harvested from the linseed plant are preferred as they present good mechanical properties combined with high availability compared to other natural fibers such as hemp or jute. Furthermore, flax fibers show similar or even higher specific

stiffness than glass fibers, and CO_2 uptake during the growth of the plant fibers balances with energy emissions during processing [2].

However, the processing of natural fibers into composite materials poses technical challenges due to their inherent hydrophilic properties and UV sensitivity. It is known that exposure to UV light lowers the mechanical properties of flax fibers [3], whereas the absorption of moisture from the environment leads to the degradation of mechanical fiber properties, swelling, formation of micro-cracks and a decrease in the interfacial strength between polymer matrix and fiber resulting in premature failure [4]. The direct surface exposure of the flax fibers should thus be avoided for better protection against chemical, physical, or mechanical degradation. Previous research showed the possibility of reducing the water sensitivity of flax by a single fiber treatment: physical pre-treatment such as gamma irradiation and ultra-sound techniques can reduce the water uptake by about 15% [5], and chemical pretreatment increases the moisture resistance [6]. Another way of increasing the environmental resistance of natural composites is to use a protective coating on the final product. As known from the wood industry, standard coatings that increase water resistance are based on waxes [7] or linseed oil [8]; they rather form a soft layer or impregnate the open cell structure of wood. Contrarily, the application conditions and compatibility of coatings with natural fiber composites might be challenging, given the differences in surface structure and more heterogeneous wetting conditions. The composites form a denser surface and are preferably used under more stringent conditions requiring a longer lifetime. Therefore, alternative coatings should provide sufficient mechanical performance (e.g., hardness, wear and scratch resistance), environmental resistance (e.g., water repellence), long-term stability (e.g., UV resistance), good compatibility and fast processing. In particular, protective bio-based coatings are needed, where properties can be adapted by selecting the composition and controlling the crosslinking conditions.

In this study, various types of bio-based coatings, including linseed oil, wax and bio-based epoxy, were applied to a flax/epoxy composite to reduce surface degradation. In particular, the crosslinking of bio-based epoxy coatings offers benefits for tuning properties towards better performance depending on the selection of resin, hardener and diluent.

2. Materials and Methods

2.1. Biocomposite Substrates

A flax fabric with a 2 × 2 twill woven structure and a density of 250 g/m^2 (Weverij Flipts en Dobbels, Roeselare, Belgium) was combined with Araldite LY 1564 SP resin and XB-3404-1 hardener (Huntsman, Basel, Switzerland). A 2D composite plate was produced using a vacuum infusion process under state-of-the-art processing conditions. The laminated composite contained 5 plies of flax fabric corresponding to a total fiber volume fraction of 35%. Testing substrates (10 × 10 cm^2) had a thickness of 3.6 mm and the surface wettability was improved by roughening it with abrasive sandpaper (grid 120).

2.2. Coating Application

The linseed oil coating consists of commercial-grade raw linseed oil that is commonly used for wood protection and is obtained in local shops (Hubo, Hasselt, Belgium). Although linseed oil is a drying oil with high reactivity and a number of double bonds for oxidative crosslinking (iodine value I.V. = 195), the selected grade also contains Mg and Zr additives to catalyse the crosslinking mechanism.

A paraffine–wax aqueous emulsion with anionic stabilization and 50% dry content was chosen as the industrial grade for the hydrophobization of wood surfaces (Govi, Gent, Belgium). Both linseed and wax coatings were applied by brushing towards two target coating thicknesses and aged for 1, 4 and 8 weeks under controlled laboratory conditions (50% RH, 23 °C), as summarized in Table 1. The coating thickness was selected in a comparative range with that of the alternative epoxy coatings developed below.

Table 1. Overview and application conditions of linseed oil and wax coatings.

Sample	Material	Dry Thickness	Aging
LO-1	Linseed oil	100 µm	1, 4, 8 weeks
LO-2	Linseed oil	300 µm	1, 4, 8 weeks
PW-1	Paraffin wax	100 µm	1, 4, 8 weeks
PW-2	Paraffin wax	300 µm	1, 4, 8 weeks

The epoxy coatings were formulated from commercially available building blocks for epoxy resin, diluent and amine crosslinkers, including fossil-based reference materials and bio-based alternatives, as summarized in Table 2. The bio-based bisphenol A diglycidyl ether (DGEBA) was synthesized from glycerol and was purchased under the brand name Greenpoxy Surf Clear (Sicomin, Chateauneuf les Martigues, France). The epoxy resin was mixed with two crosslinkers, including a fossil-based amine (FA) and a bio-based phenalkamine (PK). The FA was a mixture of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (30 to 50 wt.-%) and m-phenylene bis(methylamine) (10 to 30 wt.-%) (Resion Resin Technology, Moordrecht, The Netherlands). The PK was obtained after a reaction took place between cardanol and 1,2-ethylenediamine (Anacarda, Wigan WN, UK). The diglicydyl ether (DGE) and triglicydyl ether (TGE) were both used in two concentrations as fossil- and bio-based diluents, respectively (Merck, Darmstadt, Germany). The epoxy coatings were applied by blade coating with a 300 µm thickness and aged for 7 days under controlled laboratory conditions (50% RH, 23 °C).

Table 2. Composition of epoxy coatings including fossil-based and bio-based crosslinkers and diluents (numbers in weight percentage (wt.-%), calculated under stoichiometric ratio based on equivalent epoxy numbers (EEW) and amine numbers (AHEW)).

Sample	DGEBA Bio-Epoxy Resin	DGE Fossil-Diluent	TGE Bio-Diluent	FA Crosslinker	PK Crosslinker
EP-1	10	-	-	5 (2:1)	-
EP-2	10	-	-	-	6.25 (1.6:1)
EP-3	10	2	-	-	6.7 (1.6:1)
EP-4	10	5	-	-	7.1 (1.6:1)
EP-5	10	-	2	-	6.7 (1.6:1)
EP-6	10	-	5	-	7.1 (1.6:1)

2.3. Characterization Methods for Coated Composites

The water contact angles were determined from sessile drop tests with D.I. water using a droplet volume of 3 µL and by averaging the left and right contact angles after an elliptical fitting of the droplet geometry. The decrease in the water contact angle value over time was followed by dynamic measurements over time until the stabilization of the droplet. The microhardness was measured according to ASTM D2240 [9] using a handheld Shore D micro-indentor with a standardized hardened steel tip of 30° and a 0.1 mm tip radius. The scratching resistance was evaluated according to ISO 4586-2 [10], using a sclerometer type 3092 (Elcometer, Aalen, Germany) with a tungsten carbide tip (0.75 mm radius, 5 N load).

Abrasive wear resistance was evaluated via circular Taber abrasion testing, using calibrated CD-10 wheels under a 250 g load of 1000 cycles (ASTM D4060) [11]. The wear was subsequently determined from the weight loss of the sample. The QUV weatherability testing was performed under UVA-340 nm conditions with alternating light cycles (8 h UV at 60 °C) and condensation exposure cycles (4 h condensation at 50 °C) under light intensity of 0.76 W/m^2 (ASTM G154) [12]. The periodic evaluations were made after intervals of 500, 1000 and 2000 h. The reduction in gloss after UV exposure was measured using a trigloss meter under a 60° incident light angle (BYK-Gardener, Geretsried, Germany).

3. Results and Discussion

3.1. Performance of Linseed Oil and Wax Coating

First, the performance of linseed oil and wax coatings applied to flax/epoxy composite surfaces was evaluated as they are both known as protective coatings in the wood industry. Good surface coverage and homogeneous flow of the liquid coating after brushing were observed on the biocomposite surfaces. Hydrophobicity was evaluated based on the water contact angles recorded as a function of time (Figure 1a). For uncoated biocomposites, the ingress of water resulted in a continuous decrease in the contact angles as a function of measuring time. The water contact angles on the coated samples stabilized over time, illustrating efficient coverage of the surface; however, there were strong variations in the contact angle values depending on the ageing time of the coatings. The steady-state values after 1 min droplet contact were compared for different ageing conditions (Figure 1b). For linseed oil coatings, hydrophobic protection was not immediately obtained and the oxidative crosslinking progressed over several weeks with a consequent increase in contact angles. For paraffin–wax coatings, the migration of paraffin wax from the surface into the bulk resulted in a progressive decrease in hydrophobicity over time. In addition to the unfavourable curing time needed for expressing sufficient hydrophobic protection, the mechanical scratch resistance of linseed oil and paraffin wax coatings was very weak and showed a breakthrough under a 5 N scratching load due to the lack of crosslinking and low hardness of the coatings (Figure 1c). This corresponds to a low Shore D hardness H = 45 (sample LO-2) and H = 38 (sample PW-2) after 8 weeks of ageing, respectively.

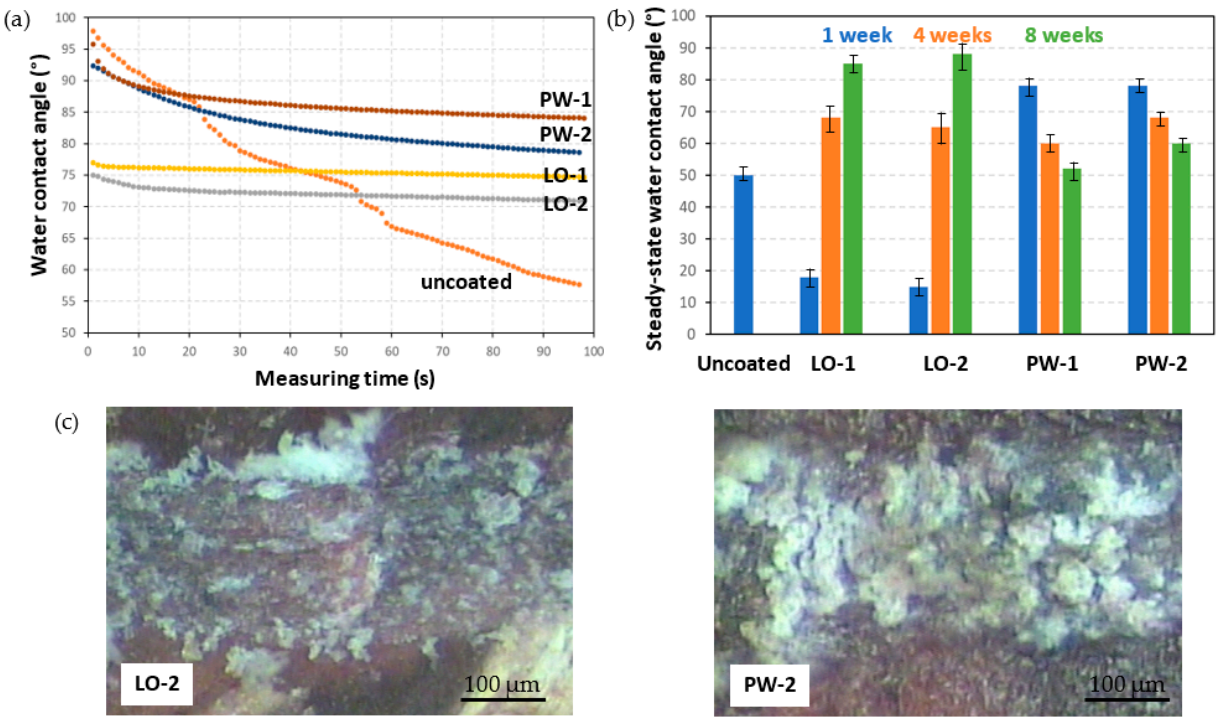

Figure 1. Evaluation of mechanical resistance and water repellence for linseed oil and wax coatings with linseed oil (LO) and paraffin–wax (PW): (**a**) water contact angle measurements, (**b**) steady-state static water contact angles after 1 min, and (**c**) scratch resistance testing under 5 N load.

3.2. Performance of Bio-Based Epoxy Coatings

The application of epoxy coatings illustrated homogeneous coverage and wetting after the sanding of the composite surface. The steady-state water contact angles for different compositions of crosslinked epoxy coatings (Figure 2a) indicate that bio-based PK crosslinkers provide a somewhat lower water contact angle compared to FA crosslinkers, which can be a result of the higher crosslinking density in the presence of PK. The high crosslinking

density of PK may result in a smaller amount of free molecular chains and less exposure of the hydrophobic groups on the coating surface. In the presence of diluents, however, hydrophobicity is mostly enhanced due to the bio-based TGE diluent in combination with the PK crosslinkers, as both contain hydrophobic moieties in their molecular structure. The high crosslinking density for epoxy coatings with a PK crosslinker is also expressed in high values of microhardness (Figure 2b) and, consequently, a better abrasive wear resistance (Figure 2c). The results indicate that the coatings have higher microhardness in the presence of bio-based diluents compared with fossil-based diluents for a similar concentration, likely due to the higher functionality and crosslinking density in the presence of a bio-based TGE diluent. However, the highest concentrations of diluents obviously cause weakening due to the more flexible molecular structure. The hardness results are further supported by scratch resistance testing (Figure 2d), where hardly any scratch damage is observed for coatings including bio-based diluents and crosslinkers with the highest microhardness. In conclusion, the coating performance depends on suitable diluents and crosslinkers, and it is directly controlled by the intrinsic mechanical properties related to the crosslinking density.

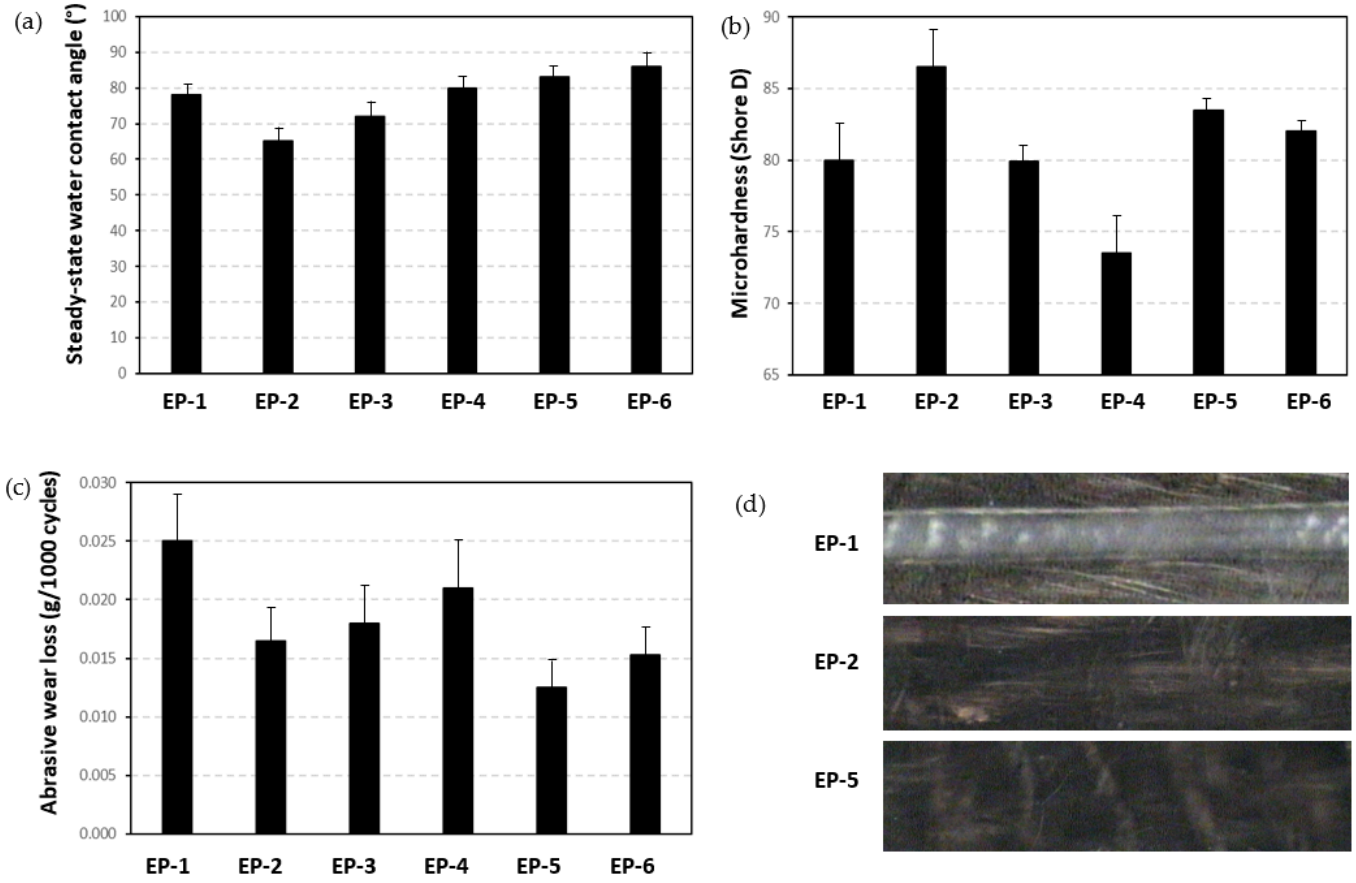

Figure 2. Physico-chemical and mechanical test results of crosslinked epoxy coatings on biocomposite substrates: (**a**) average static water contact angle, (**b**) micro-hardness, (**c**) abrasive wear after Taber testing, and (**d**) scratch resistance testing under a 5 N load.

The results of UV resistance (Figure 3) indicate the favorable effects of the PK crosslinker and bio-based diluents, offering the smallest decay in properties. The migration of free diluents after 250 h of exposure may offer hydrophobic protection against further degradation. In addition, the high hydrophobicity and water repellence of the bio-based diluents form the first barrier against weathering effects. In general, the better performance of the PK versus FA crosslinker in UV resistance is in line with the improved mechanical properties.

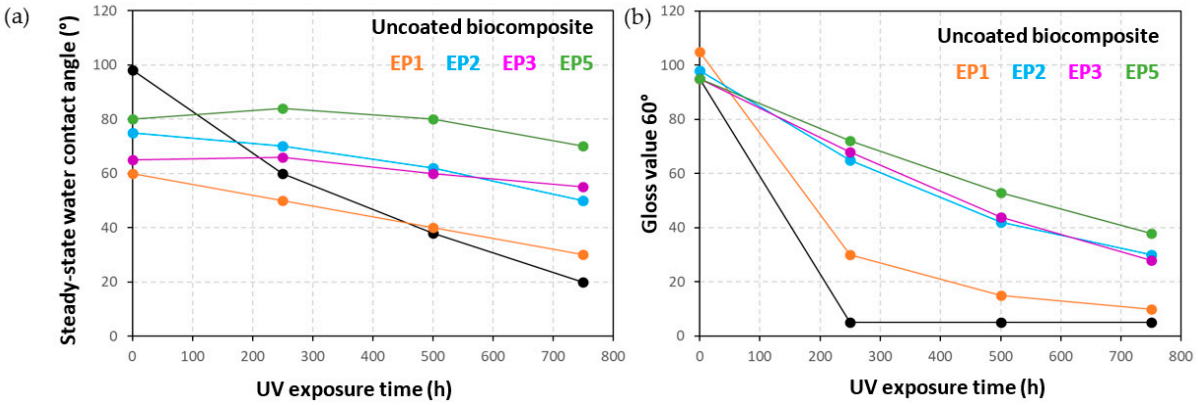

Figure 3. Degradation of epoxy coating properties on a biocomposite substrate after UV exposure as a function of time: (**a**) water contact angle decrease, and (**b**) gloss reduction.

4. Conclusions

The linseed oil and wax coatings developed only instable hydrophobic protection and present weak mechanical resistance, whereas alternative coatings with bio-based epoxy resin, diluents and crosslinkers offer better protection and good compatibility with a biocomposite surface. The required performance of bio-based epoxy coatings can be tuned by the composition and crosslinking conditions, where high mechanical resistance, hydrophobicity and weathering resistance are demonstrated in the presence of bio-based phenalkamine crosslinkers and triglicydyl ether diluents.

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