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Phosphonated and methacrylated biobased cardanol monomer:

Synthesis, Characterization and Application

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Abstract

To create adhesive coatings, biobased phosphorylated monomer from cardanol was synthesized and polymerized by UV curing or miniemulsion radical polymerization. Phosphonic ethoxy cardanol methacrylate (CMP) was synthesized from cardanol via hydroxyethylation, followed by phosphorylation radical addition of dimethyl phosphite onto the unsaturations of the C15 aliphatic chain of cardanol prior methacrylation of the hydroxyl ethoxy group. Lastly the cleavage of the phosphonate ester groups was made to generate the targeted phosphonic acid moieties as adhesion promoters. Moreover, the development of a phosphonic latex was successfully achieved by miniemulsion radical copolymerization in water with an additional redox termination to ensure quantitative monomer conversions. Phosphonic cardanol and cardanol (as reference) latexes were characterized by dynamic light scattering. The effects of cardanol derivatives on the performance of protective coatings on steel plates were evaluated in UV-cured coatings as well as in latex coatings in terms of contact angle and adhesion effectiveness. In coatings, increased hydrophobic properties were observed in formulations containing free cardanol or cardanol methacrylate. On the other side, the incorporation of phosphonic acid groups onto cardanol significantly improved the adhesion effectiveness of the coating, whatever the film-making technique.

Keywords

Cardanol; phosphorylation; coatings; adhesion; UV-curing; miniemulsion radical polymerization

Introduction

A large part of key commercial chemicals consists of aromatic substances derived from petrochemical resources.¹ In recent years, the demand for renewable resource-derived polymers has increased dramatically owing to increasing environmental concerns and restricted availability of fossil resources.² Cardanol is a by-product produced from cashew nut shell liquid (CNSL), which is directly extracted from the shell of the cashew nut, fruit from the cashew tree, *anacardium occidentale*, mostly grown in India, East Africa, and Brazil³. The global production of CNSL approaches one million tons annually and CNSL became one of the few major and economic sources of naturally occurring phenols. This promising aromatic renewable resource represents a good natural alternative to petrochemical-derived phenols⁴. The thermal treatment of CNSL followed by a distillation leads to the decarboxylation of anacardic acid (main constituent of CNSL) that yields an industrial grade of cardanol (approximately 90%), with a small quantity of cardol and methylcardol.^{5,6} Cardanol is a yellow, pale liquid composed of four meta-alkyl phenols differing by degrees of unsaturation of the aliphatic chain (Figure 1): saturated chains (SC) 7 %, monoolefinic (MO) 48 %, diolefinic (DO) 16 % and triolefinic (TO) 29 % of chains.^{7,8} The phenolic character of cardanol and the unsaturations in its hydrophobic alkyl side chain attracted attention for the various possible chemical modifications they allow, and make it an important reactive starting material having potential industrial applications such as antioxidants,^{9,10} plasticizers,^{11,12} flame retardants,^{13,14,15} and resins.¹⁶⁻¹⁹

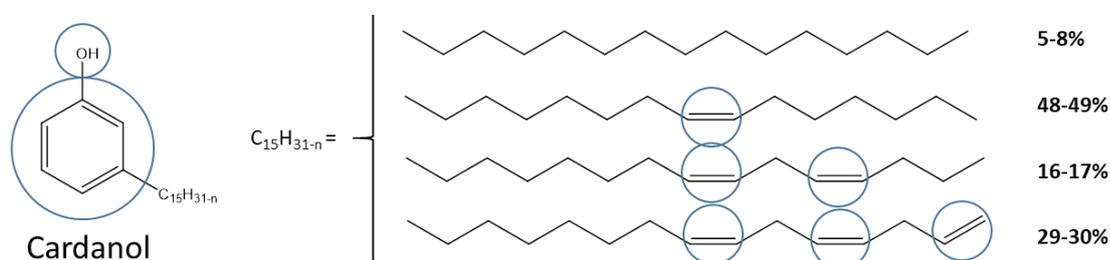


Figure 1 : Structure of cardanol

In the field of coatings, cardanol could provide interesting new properties. The unique structure of cardanol imparts many properties²⁰ to the resulting copolymers, such as

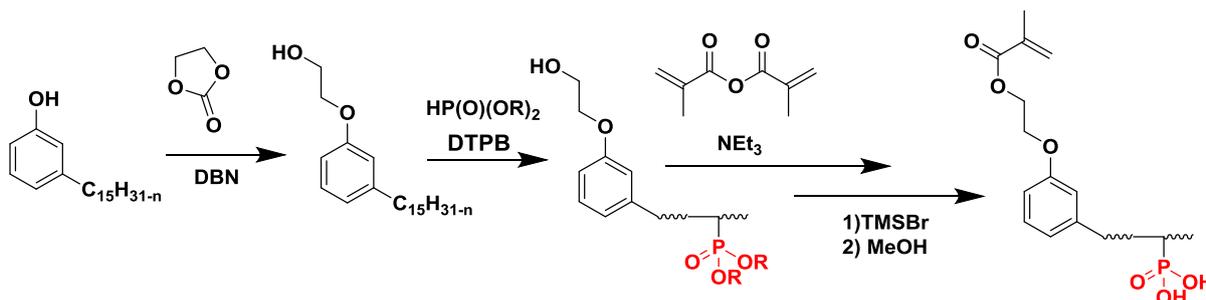
flexibility, hydrophobicity, and acid/alkali resistance. The generation of new efficient protective coatings is indeed a challenge for the scientific community. Organic coatings are widely used for paints, such as methacrylates, polyurethanes or epoxy resins with good adhesion to metal substrates, high chemical resistance, and long-term corrosion resistance.²¹

Cardanol derivatives have been widely used as epoxy²²⁻²⁵-based or polyurethane^{26,27} organic coatings. However, UV-cured coatings or aqueous latex-based coatings are more ecological and efficient methods as they require lower energy consumption. UV curing produces a film instantly by fast cross-linking reactions without major modification of the film thickness. For this technique, highly reactive functional groups are used, such as vinyl groups including acrylate or methacrylate functions. Polymer latex (from the same (meth)acrylate monomers) can form films via particle coalescence. The zero-VOC (volatile organic compound) process and the reduction of the minimum film formation temperature are of particular interest in this pathway. To our knowledge, only our team has worked on the emulsion polymerization of cardanol methacrylate monomers. Latexes prepared by emulsion²⁸ or miniemulsion²⁹ polymerizations were produced and fully characterized, and cardanol-containing methacrylate monomer showed good copolymerization reactivity with methyl methacrylate or oleic soybean oil monomer.³⁰ Cardanol-based acrylates were classically prepared by the chemical modification of the unsaturation of the side chain^{31,32} but recently, different teams suggested the acrylation of the phenol via acryloyl chloride³³ directly on cardanol or on the product of cardanol-epichlorohydrin.^{28,34} Our team proposed the hydroxyethylation of the phenolic hydroxyl group followed by methacrylation using methacrylic anhydride. A biobased reactive diluent, cardanyl acrylate, was synthesized from cardanol and used to modify a castor oil-based polyfunctional polyurethane acrylate (PUA) resin.³³

The aim of the present paper is to prepare new cardanol-based methacrylate able to promote adhesion and enhanced barrier properties to metal surfaces and amenable to UV-crosslinking or polymerization in aqueous dispersed media.

The first step consists in the chemical modification of cardanol with a radically polymerizable group to favour its incorporation into the UV coating network or into latexes and the second step involves the addition of functional groups on the alkyl side chain to impart adhesive and surface properties to the polymer coating (Scheme 1). Phosphonic acids were chosen to

provide adhesive properties and corrosion inhibition to the films. Indeed, academic research highlighted *N,N*-amino-bisphosphonic-containing methacrylates³⁵ and gem-bisphosphonic-containing methacrylates³⁶ as efficient adhesion promoters (on steel surfaces). In addition, phosphonated fatty acids were shown to significantly enhance the anticorrosion performance of the coating as a result of improved barrier properties on metallic sheets.³⁷ Recently, phosphoric functions were grafted on epoxy cardanol via ring-opening reaction of the epoxy group in the alkyl chain of cardanol.³⁸



Scheme 1: General strategy of the synthesis of phosphonated cardanol methacrylate

Cardanol-containing phosphonated methacrylates were chosen to examine the effect of the C15 aliphatic chain, and because phosphonic functions are much less prone to hydrolysis than phosphoric ones. Methacrylates were chosen for their longer shelf life compared to acrylates.

Materials and Methods

Reagents

Cardanol NX2026 containing 1 % cardol was kindly supplied by Cardolite. Dimethyl phosphite (DMP, 98%, Aldrich), di-tert-butyl peroxide (98%, Aldrich), ethylene carbonate (98%, Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%, Aldrich), triethylamine (99.5%, Aldrich), methacrylic anhydride (94%, Aldrich), sodium hydroxide (NaOH, 98%, Aldrich), sodium sulfate (Na_2SO_4 , >99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DPAP, 99%, Aldrich), methanol (MeOH, >99%, Aldrich), ethyl acetate (>99%, VWR), trimethylbromosilane (TMSBr, 97%, Aldrich), sodium dodecyl sulfate (SDS, >99%, Aldrich), ammonium persulfate (APS, >99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich), hexadecane (>99%, Aldrich), 1,4-bis(trimethylsilyl)benzene (BTMSB, 96%, Aldrich), *tert*-butylperoxybenzoate (<95%, Aldrich), ascorbic acid (>99%, Aldrich), tripropylene glycol diacrylate (>82.5%,

Aldrich), 1,6-hexanediol diacrylate (80%, Aldrich), 2-hydroxy-2-methylpropiophenone (Darocur 1173, 97%, Aldrich), sodium bicarbonate (NaHCO_3 , 99.7%, Aldrich), 2,2'-azobis(2,4-dimethyl valeronitrile) (V-65, 95%, Wako), and toluene (99%, Aldrich) were used as received. Dichloromethane was dried with molecular sieves (4 Å, 2.5-5.0 mm beads (4-8 Mesh), Fisher Chemical) and kept under N_2 before use. Deionized water (DIW) ($1 \mu\text{S cm}^{-1}$) was obtained using a D8 ion exchange demineralizer from A2E (Affinage de L'Eau).

Synthesis of ethoxy cardanol

Ethoxy cardanol was synthesized according to the procedure reported in a previous paper.²⁹ Cardanol and ethylene carbonate were combined in a round-bottom flask and heated to 150 °C, at which point a one-shot injection of DBN was added. The solution was left to react for 30 min at 150 °C, then 4 – 6 hours at 180 °C.

Radical phosphorylation of ethoxy cardanol

Thermal Radical Addition

Ethoxy cardanol (10.0 g, 29 mmol, 1 eq.) and dimethyl phosphite (35.0 g, 320 mmol, 11 eq., 5.5 eq. to cardanol C=C bonds) were combined in a 2-neck round-bottom flask equipped with a magnetic stir bar and sealed with a septum. The resulting mixture was purged with nitrogen for 30 min. Di-tert-butyl peroxide (DTBP) (3.0 mL, 3.5 mmol) was purged with nitrogen for 5 min. The reaction flask was immersed in a 140°C oil bath and 0.6 mL of di-tert-butyl peroxide was injected into the solution via a syringe. The remaining di-tert-butyl peroxide was divided into 4 batches of 0.6 mL and injected into the reaction mixture at 1.5 h intervals. The reaction proceeded for 24 h and samples were withdrawn periodically and analyzed by ^1H NMR and ^{31}P NMR. The final mixture was washed three times with 0.01 M NaOH solution and once with DIW. The recovered organic phase was dried with Na_2SO_4 , filtered, and the solvent was removed by rotary evaporator at 30°C under vacuum. The product was obtained as a viscous brown liquid with a yield of 40% after washing.

^1H NMR: Figure S1, (400 MHz, CDCl_3 , δ , ppm): 7.20 (t, 1H, aromatic proton 3), 6.70–6.85 (m, 3H, aromatic protons 2, 4, and 6), 5.75–5.90 (m, 1H, C_{15} chain, proton i), 5.30–5.50 (m, C_{15} chain, internal double bond protons h), 4.95–5.15 (m, 2H, C_{15} chain, protons of the terminal double bond g), 4.38 (t, 2H, protons v'), 4.13 (t, 2H, protons u'), 4.05 (t, 2H, protons v), 3.91 (t, 2H, protons u), 3.58-3.83 (m, 3H, -P-O- CH_3 , phosphonate protons k), 2.83 (m, 2H, C_{15}

chain, protons f), 2.60 (t, 2H, C₁₅ chain, protons e), 2.00–2.15 (m, 2H, C₁₅ chain, protons d), 1.64 (m, 2H, C₁₅ chain, protons c), 1.20–1.50 (m, C₁₅ chain, protons b,b'), 0.92 (m, 3H, C₁₅ chain, terminal -CH₃, protons a, a').

³¹P NMR: Figure S2, (400 MHz, CDCl₃, δ, ppm): 33.3-39.0 (m, -CH₂-PO-)

UV Irradiation Radical Addition

2,2-Dimethoxy-2-phenylacetophenone (4.8 g, 19 mmol, 0.5 eq.) was dissolved in dimethyl phosphite (30.0 g, 273 mmol, 8.3 eq.) in a round-bottom flask. Ethoxy cardanol (11.4 g, 33 mmol, 1 eq.) was added to the mixture and the solution was purged with nitrogen for 30 min. The reaction mixture was transferred to a quartz tube with a magnetic stir bar and purged with nitrogen for an additional 15 min. The tube was sealed with a septum secured with parafilm and placed into a UV reactor equipped with 16 lamps. The reaction proceeded under agitation with UV irradiation at λ=300 nm for 24 h at 40°C. Samples were withdrawn periodically and analyzed by ¹H NMR and ³¹P NMR. The final mixture was washed three times with 0.01 M NaOH solution and once with DIW. The recovered organic phase was dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporator at 30°C under vacuum. The product was obtained as a brown, viscous liquid with a yield of 80% after washing.

¹H NMR: Figure 1, (400 MHz, CDCl₃, δ, ppm): 7.23-8.1 (m, aromatic protons of initiator DPAP), 7.20 (t, 1H, aromatic proton 3), 6.70–6.85 (m, 3H, aromatic protons 2, 4, and 6), 5.75–5.90 (m, 1H, C₁₅ chain, proton i), 5.30–5.50 (m, C₁₅ chain, internal double bond protons h), 4.95–5.15 (m, 2H, C₁₅ chain, protons of the terminal double bond g), 4.05 (t, 2H, protons v), 3.91 (t, 2H, protons u), 3.58-3.83 (m, 3H, -P-O-CH₃, phosphonate protons k), 2.83 (m, 2H, C₁₅ chain, protons f), 2.60 (t, 2H, C₁₅ chain, protons e), 2.00–2.15 (m, 2H, C₁₅ chain, protons d), 1.64 (m, 2H, C₁₅ chain, protons c), 1.20–1.50 (m, C₁₅ chain, protons b,b'), 0.92 (m, 3H, C₁₅ chain, terminal -CH₃, protons a, a').

³¹P NMR: Figure S3, (400 MHz, CDCl₃, δ, ppm): 33.3-39.0 (m, -CH₂-PO-)

The percentage of phosphorylation was calculated using ¹H NMR with equation 1.

$$\% \text{ phosphorylation} = \left(1 - \frac{\left[\int_{4.96}^{5.17} C=C + \int_{5.43}^{5.56} C=C + \int_{4.61}^{4.78} C=C \right]_t}{\left[\int_{4.96}^{5.17} C=C + \int_{5.43}^{5.56} C=C + \int_{4.61}^{4.78} C=C \right]_{t=0}} \right) \times 100\% \quad (1)$$

Synthesis of ethoxy cardanol methacrylate (CM)

Ethoxy cardanol methacrylate (CM) was synthesized according to the procedure reported in a previous paper.²⁹ Ethoxy cardanol, dry dichloromethane, and triethylamine were combined in a round bottom flask in an ice bath and purged with nitrogen for 30 min. Methacrylic anhydride, previously purged with nitrogen, was added dropwise into the reaction solution over 10 min to begin the reaction. The reaction proceeded for 18 hours in an ice bath.

Synthesis of phosphonic ethoxy cardanol methacrylate (CMP)

Phosphonated ethoxy cardanol (14.1 g, 31 mmol, 1 eq.) was mixed with dry dichloromethane (45 mL) and triethylamine (16 mL, 114 mmol, 3.7 eq.) in a round-bottom flask, subsequently sealed with a septum, and placed into an ice bath. The reaction mixture was purged with nitrogen for 30 min under agitation, after which methacrylic anhydride (11 mL, 130 mmol, 4.2 eq.) was purged with nitrogen for 10 min and added dropwise into the reaction mixture over 10 min. The reaction proceeded for 18 h in an ice bath. The final mixture was washed three times with 0.01 M NaOH solution and once with deionized water, then extracted with ethyl acetate. The recovered organic phase was dried with Na₂SO₄, filtered, and the solvent was removed by rotary evaporator at 30 °C under vacuum to obtain phosphonated ethoxy cardanol methacrylate as a viscous brown liquid (yield = 80%).

An ester cleavage was subsequently performed to obtain the phosphonic acid form of this compound. Phosphonated ethoxy cardanol methacrylate (10.8 g, 20.7 mmol) was dissolved in dry dichloromethane (80 mL) in a round-bottom flask with a magnetic stir bar and immersed into a 25°C water bath. Trimethylbromosilane (2.5 eq. with respect to phosphonate groups) was added dropwise into the solution at 25°C under agitation at 250 rpm. The reaction was left to proceed for 16 h with conversion measured by ¹H NMR. This intermediate product was isolated by removing the solvent using a rotary evaporator at 30°C under vacuum. Methanol was then added to the product and left under agitation for a minimum of 2 h. The final product was purified by solvent removal using a rotary evaporator at 30°C under vacuum. Phosphonic ethoxy cardanol methacrylate (CMP) was obtained in quantitative yield as a dark brown, viscous liquid and analyzed by ¹H NMR and ³¹P NMR.

^1H NMR: Figure 1, (400 MHz, CDCl_3 , δ , ppm): 7.23-8.1 (m, aromatic protons of initiator DPAP), 7.20 (t, 1H, aromatic proton 3), 6.70–6.85 (m, 3H, aromatic protons 2, 4, and 6), 6.17 (s, 1H, methacrylate proton z), 5.75–5.90 (m, 1H, C_{15} chain, proton i), 5.57 (s, 1H, methacrylate proton z'), 5.30–5.50 (m, C_{15} chain, internal double bond protons h), 4.95–5.15 (m, 2H, C_{15} chain, protons of the terminal double bond g), 4.42-4.66 (m, 1H, -P-OH, phosphonic acid protons j), 4.05 (t, 2H, protons v), 3.91 (t, 2H, protons u), 2.83 (m, 2H, C_{15} chain, protons f), 2.60 (t, 2H, C_{15} chain, protons e), 2.00–2.15 (m, 2H, C_{15} chain, protons d), 1.98 (s, 3H, methacrylate -CH₃, protons y), 1.64 (m, 2H, C_{15} chain, protons c), 1.20–1.50 (m, C_{15} chain, protons b,b'), 0.92 (m, 3H, C_{15} chain, terminal -CH₃, protons a, a').

^{31}P NMR: Figure S4, (400 MHz, CDCl_3 , δ , ppm): 39.8 (m, -CH₂-P-OH)

Solution copolymerization of methyl methacrylate (MMA) and phosphonic ethoxy cardanol methacrylate (CMP)

The solution copolymerization of CMP and MMA was carried out to low conversions to study the copolymerization behavior of the two monomers. CMP (5 g, 10 mmol) and MMA (5 g, 50 mmol) were combined with V-65 (0.2 g, 0.8 mmol, 2 wt.% with respect to monomers) and 1,4-BTMBS (0.3 g, 1.4 mmol, 3 wt.% with respect to monomers) in toluene (35 g) in a round-bottom flask with a magnetic stir bar and sealed with a septum. The reaction mixture was purged with argon in an ice bath for 30 min under magnetic stirring. The polymerization began by immersing the flask into an oil bath thermostated at 70°C. The reaction proceeded for 6 h under agitation. Samples were withdrawn periodically.

Synthesis of latex coatings

Miniemulsion radical homopolymerization of ethoxy cardanol methacrylate (CM)

The miniemulsion copolymerization of CM and MMA was carried out according to the procedure in a previous article²⁹ with a 50:50 weight ratio of CM to MMA to prepare a 20 wt.% solids P(CM₅₀-co-MMA₅₀) latex.

Miniemulsion radical copolymerization of phosphonic ethoxy cardanol methacrylate (CMP) and methyl methacrylate (MMA)

The miniemulsion copolymerization of CMP with MMA to prepare a 10 wt.% solids P(CMP₅₀-co-MMA₅₀) latex was carried out using a similar procedure as the P(CM) latex. A 250 mL double-walled glass reactor equipped with a U-shaped glass stirring rod was heated to 70 °C

and filled with argon. In a glass vial, MMA (1.25 g, 12.5 mmol) and CMP (1.25g, 2.5 mmol) were mixed with hexadecane (0.14 g, 0.62 mmol, 5.5 wt.% with respect to monomers), V-65 (0.05 g, 0.2 mmol, 2 wt.% with respect to monomers), 1,4-BTMSB (0.075 g, 0.34 mmol, 3 wt.% with respect to monomers), and *tert*-butylperoxybenzoate (0.025 g, 0.12 mmol, 1 wt.% with respect to monomers), sealed with a septum, and purged with argon for 15 min under agitation in an ice bath. In a separate beaker, SDS (0.125 g, 0.43 mmol, 5 wt.% with respect to monomers) and NaHCO₃ (0.025 g, 0.3 mmol, 1 wt.% with respect to monomers) were mixed with deionized water (17.5 g, previously purged with argon) under magnetic stirring. A macroemulsion was formed by adding the organic phase to the aqueous solution under high shear for 30 min under argon bubbling in an ice bath. The resulting macroemulsion was sonicated using a BioBlock Scientific Vibracell 75043 equipped with a CV33 probe (13 mm diameter) at 60% power for 3 minutes in an ice bath, under agitation and argon bubbling. The resulting miniemulsion was then transferred to the heated glass reactor and the copolymerization was carried out under argon atmosphere and agitation at 300 rpm for 6 h at 70 °C. After 4 h of reaction, ascorbic acid (0.01 g, 0.06 mmol) was added dropwise into the reaction mixture via a syringe over 30 min to ensure quantitative monomer conversion.

Coating formulation and application on steel plates

A bar coater (SHEEN Automatic Film Applicator 1133N) was used to evenly apply a thin layer of coating on the steel substrates (R35 steel plates from Labomat). The R35 steel plates are cold-rolled and pretreated, measuring 76 mm × 127 mm. The bar used was for a 20 μm thick film and the speed was set to 80 mm/s.

For UV-cured coatings, a base formulation consisting of Darocur 1173 (6 wt.% of total formulation) and a 50:50 weight ratio of tripropylene glycol diacrylate and 1,6-hexanediol diacrylate was prepared. Different polymer coating formulations were prepared by adding functionalized cardanol to this base formulation at 5 wt.% of the total formulation. The coatings were subsequently photo-crosslinked using a UV-curing conveyor system from Fusion UV Systems, Inc. This system is equipped with a F300S UV mercury vapor lamp (1800 mW/cm²) and emits UV light in the range of 200-600 nm with a power rating of 300 W/in². The steel plates were passed 3 times under the UV light at the second speed setting of the machine (1.85 cm/s). The final coatings after curing were approximately 30 μm thick.

For latex coatings, neutralization of the latex with sodium bicarbonate was performed if the pH of the final latex was too acidic (pH>5) prior to application to avoid premature corrosion. The treated latexes were then applied onto the steel plates and subsequently dried in an oven for 8 h at 80 °C. The final coatings after drying ranged from 3 to 82 µm thick.

Characterization

Nuclear Magnetic Resonance Spectroscopy

Chemical structures of functionalized cardanol were determined by ¹H NMR and ³¹P NMR on a Bruker Avance 400 MHz spectrometer at room temperature. External reference was trimethylsilane (TMS) with chemical shifts given in ppm. Approximately 0.1 mL of the reaction solution were withdrawn via syringe and placed into an NMR tube and diluted with 0.5mL of CDCl₃. The phosphorylation of cardanol was monitored by ³¹P NMR; to adjust for the functionalized cardanol, the D1 was increased to 12.5 s to obtain quantitative ³¹P NMR results.

FTIR

The complete conversion of the photo-crosslinking reaction of the polymer coatings prepared using the UV-curing conveyor system were confirmed by FTIR analysis on a Thermo Scientific Nicolet 6700 FTIR. The spectra were analyzed using an OMNIC Series 8.2 software from Thermo Scientific. The conversion was determined by following the intensity of IR absorption bands of the methacrylate monomer double bond.

Coating thickness

The thickness of the polymer coatings were analyzed using a BykoTest from Byk Instruments and double-checked with a POSiTest DFT from DeFelsko Corporation. The error associated with the POSiTest DFT is +/- 2 µm + 3% of the measurement. An average of nine points across the surface of the coating is reported.

Adhesion test

Adhesion test was performed with a TQC Cross cut adhesion test kit CC3000 from TQC Sheen following the ASTM D3359 - ISO 2409 norm.

Contact angle measurements

Contact angle measurements were performed on a contact angle system OCA15Pro from Data Physics equipped with an electronic syringe unit. Measurements were performed using

the sessile drop method with deionized water at 25 °C and contact angles were measured using the SCA20 software.

Dynamic light scattering (DLS)

Dynamic light scattering particle size measurements were performed on a Vasco 3 nanoparticle size analyzer from Cordouan Technologies at 25 °C using the cumulant model. The laser power, time interval, and number of channels were modified accordingly to obtain a good ACF (autocorrelation function). Standard deviation (less than 10%) is given for each measurement. Samples for DLS measurements were prepared by diluting one drop of latex in 5 mL of deionized water. An average of 10 measurements was taken.

Results and discussion

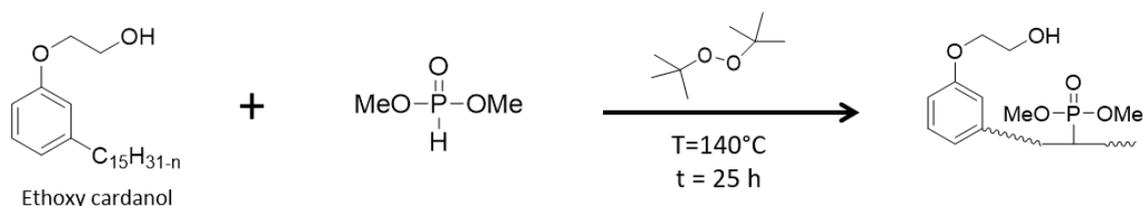
Synthesis of cardanol derivatives

Four cardanol derivatives were prepared. The general strategy for the synthesis of phosphonated cardanol methacrylates is depicted in Scheme 1. The phosphonic acid group is known for promoting adhesion to metal substrates, and therefore provide improved barrier properties for protective coatings.

The synthesis of ethoxy cardanol methacrylate has been previously discussed in a previous article.²⁹ Two methods of phosphorylation of the unsaturations of the C15 side chain of ethoxy cardanol²⁹ were investigated, i) the thermal radical addition of DMP at high temperature and ii) the UV irradiation radical addition. The phosphorylation was carried out before the methacrylation step because methacrylate groups are sensitive to high temperatures.

The main reaction for introducing phosphorus-containing moieties onto cardanol or its derivatives is the Williamson reaction, to yield phenolic phosphate esters.³⁹ Another synthesis of importance is the preparation of phosphoric acid esters of cardanol by reaction with P₂O₅, H₃PO₄ or POCl₃ onto the phenol.^{39,40} The radical phosphorylation of the double bonds of the C₁₅ alkyl chain cannot be performed directly on cardanol because of the phenol group, which inhibits radical reaction. By moving the hydroxyl group further away from the phenyl ring, the radicals produced by the initiator will be able to react with dimethyl phosphite. To move the OH group away from the phenyl, a hydroxyethylation was performed using ethylene carbonate and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) at 150-180

°C as previously described.²⁹ The phosphorylation of ethoxy cardanol, via thermal radical addition was carried out at high temperature using di-tert-butyl peroxide as thermal initiator (Scheme 2). The reaction was monitored by ¹H and ³¹P NMR for 25 h. Five additions of DTBP were made during the 25 h period.



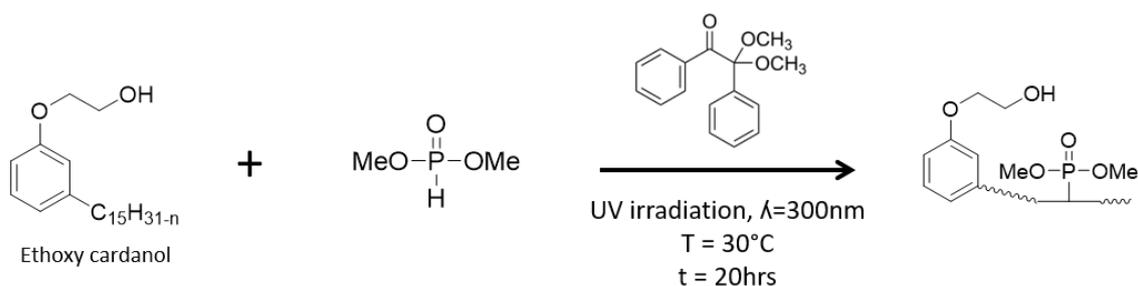
Scheme 2: Phosphorylation of ethoxy cardanol by thermal radical addition.

Figure S1 shows the ¹H NMR spectrum of the product resulting from this addition reaction.

The phosphorylation of the C15 alkyl chain was evidenced by the decrease of the ¹H NMR signals of the C=C bonds (at 4.6 to 5.6 ppm) and the appearance of a new signal assigned to the -OCH₃ group of the dimethyl phosphonate adduct at 3.7 ppm (Figure S1). The ³¹P NMR spectrum (Figure S2) also confirmed the formation of a P-C bond (at 33.3-39.0 ppm) of the phosphonate on the modified cardanol. A phosphorylation ratio of 50% (equation 1) was achieved in 25 h and the mixture of phosphonated and non-phosphonated ethoxy cardanol was obtained in relatively low yield (40%). An important loss was likely due to washing by liquid-liquid extraction to purify the product; this step could be improved by using flash chromatography. Remarkably, the signals of the two methylene groups of the hydroxyl ethoxy moiety are shifted from 3.9 and 4.0 ppm to 4.1 and 4.4 ppm in the phosphonated product. These chemical shifts suggest that the phosphite specie did not only add onto the C=C bonds of the C15 alkyl chain but also reacted with the OH group. The mechanism for this reaction remains unclear, but might be ascribed to a transesterification caused by the high temperature used and leading to cardanol methyl phosphonate -CH-P(O)(OMe)(OC₂H₄-cardanol) and/or dicardanol phosphonate -CH-P(O)(OC₂H₄-cardanol)₂. These forms could explain the different signals around 33-39 ppm on the ³¹P NMR analysis (Figure S3) and the two signals u' (4.13 ppm) and v' (4.38 ppm) in ¹H NMR analysis (Figure S1). Indeed a downfield shift in the ¹H NMR spectrum was observed for two peaks characteristic of the ethoxy of cardanol having undergone a change in their chemical environment (from

cardanol-**CH₂-CH₂**-OH to cardanol-**CH₂-CH₂**-O-P(O)(OR)(CH-)). In any case, the replacement of the hydroxyl group of ethoxy cardanol by a phosphonate prevents the methacrylation step.

To avoid these side reactions, a low temperature phosphorylation method which does not rely on DTBP was used.⁴¹ A photo-initiated radical addition was implemented as depicted in Scheme 3. As for the thermal radical phosphorylation, the photoinitiated radical addition was carried out in neat conditions since the dimethyl phosphite and ethoxy cardanol are mutually miscible. The ¹H NMR spectrum (Figure 1) of the phosphonated ethoxy cardanol under UV irradiation at 300 nm for 20 h shows that the signals for the two methylene groups of the hydroxyl ethoxy moiety remained unchanged after the reaction. This indicates that the dimethyl phosphite only reacted with the C=C bonds and that the hydroxyl group remained untouched and readily available for methacrylation. The ³¹P NMR spectrum (Figure S3) of the product resulting from the UV-mediated addition confirmed the formation of the P-C phosphonate bond with the appearance of a new signal at 33.3-39.0 ppm. A phosphorylation of 50 % of the C=C double bonds on the crude reaction product and a yield of 80% after washing were achieved. The purification step allowed for the removal of the excess phosphite reagent and the non-functionalized ethoxy cardanol. Thanks to the NMR calculation of the phosphorylation reaction conversion, each cardanol molecule has at least one phosphonate function on the alkyl chain, except the saturated chain.



Scheme 3: Phosphorylation of ethoxy cardanol by UV irradiation radical reaction.

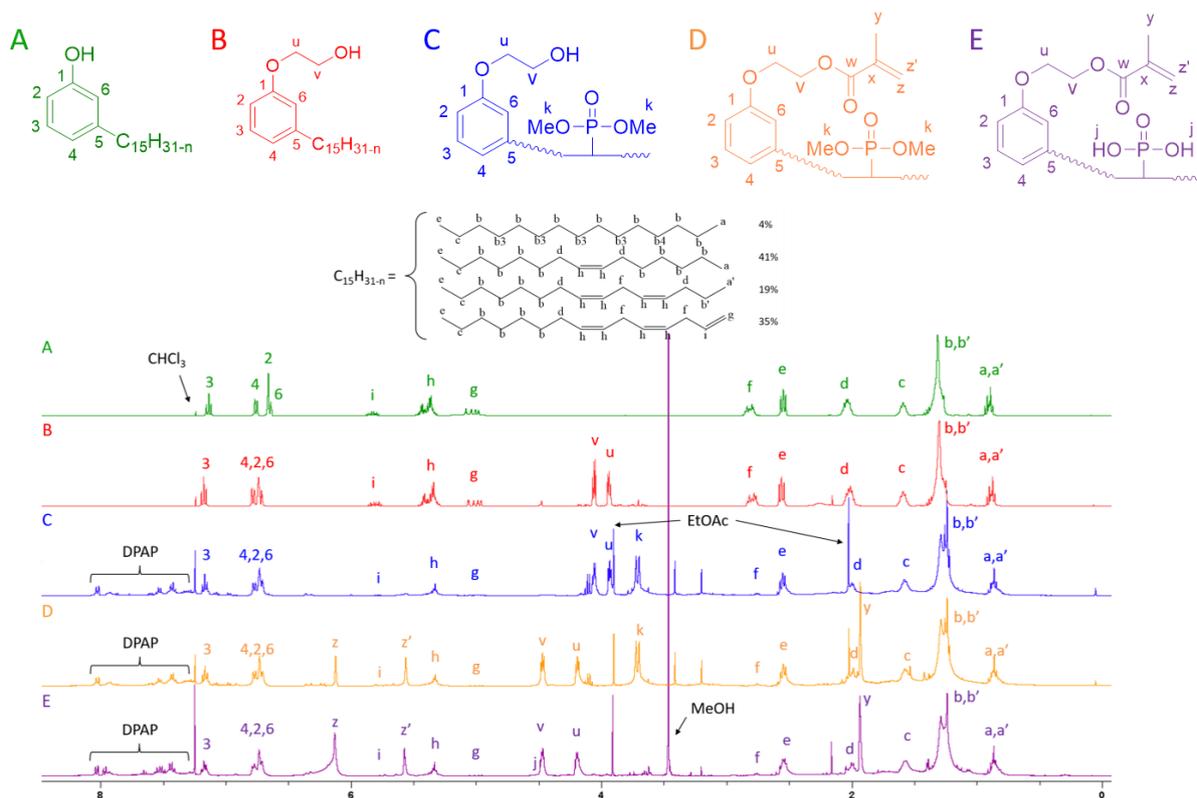
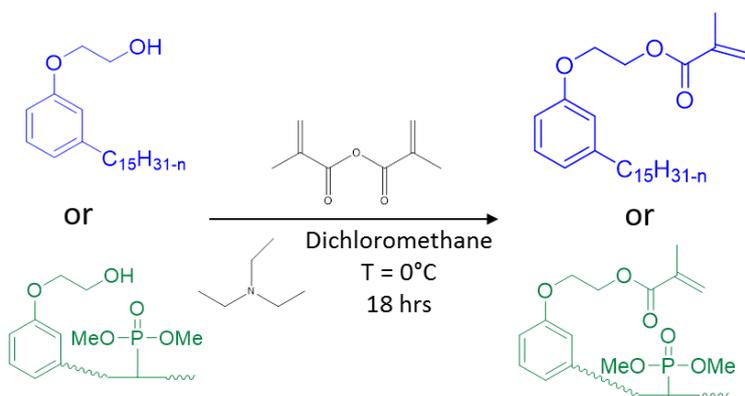


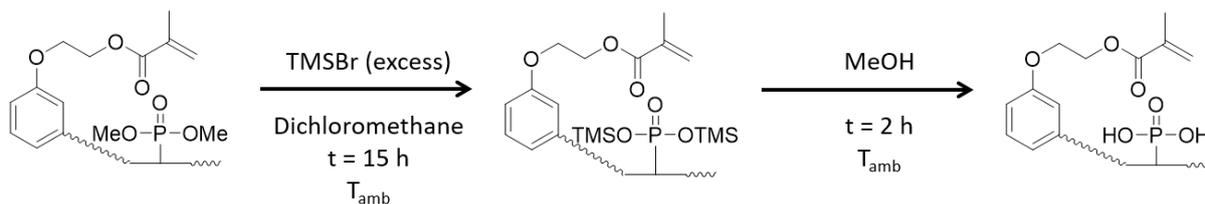
Figure 1: ^1H NMR spectra in CDCl_3 of: A: cardanol, B: ethoxy cardanol, C: phosphonated ethoxy cardanol via UV-mediated addition, D: phosphonated ethoxy cardanol methacrylate, E: phosphonic ethoxy cardanol methacrylate.

The methacrylations of the ethoxy cardanol and phosphonated ethoxy cardanol were carried out to produce functional cardanol-based vinyl monomers using methacrylic anhydride (Scheme 4). As seen in Figure 1, the methacrylation of the phosphonated ethoxy cardanol was successful: new methacrylate peaks appeared at 5.5 ppm and 6.1 ppm, and the two CH_2 signals (ethoxy group) were shifted from 3.84 and 3.98 ppm to 4.13 and 4.41 ppm respectively. A conversion of 96% was achieved after 18 h. Similarly, 95% conversion was achieved for the methacrylation of ethoxy cardanol after 18 h.



Scheme 4: Methacrylation of ethoxy cardanol and phosphonated ethoxy cardanol.

The final step of the phosphonic ethoxy cardanol methacrylate syntheses was the cleavage of the ester bonds of the phosphonate groups to form phosphonic acids as shown in Scheme 5.



Scheme 5: Ester cleavage of phosphonate to phosphonic diacid using TMSBr in dichloromethane followed by methanolysis of the phosphorylated ethoxy cardanol methacrylate.

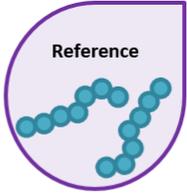
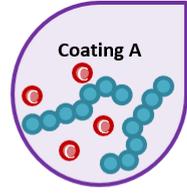
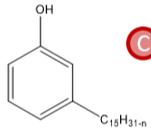
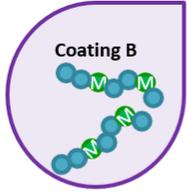
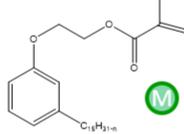
After 15 h of reaction with TMSBr in dichloromethane, the conversion of the -OMe groups into -OTMS groups was complete as seen in the reduction of the NMR signals at 3.6 ppm of the methoxy group and the apparition of a new signal at 0 ppm corresponding to the nine protons of the trimethylsilyl group. The subsequent methanolysis step led to the disappearance of the -OTMS signal at 0 ppm. The ester cleavage was completed with 96% conversion and 100% yield. The ¹H NMR spectrum in Figure 1 shows the final phosphonic ethoxy cardanol methacrylate (CMP). ³¹P NMR analysis (Figure S4) confirmed the completion of the reaction with a shift of the signal from 24.03 ppm to 39.86 ppm.

Preparation and characterization of UV-cured protective coatings

The use of photocurable materials for coating applications is advantageous because it is more eco-friendly and energy-efficient than traditional solvent-based processes. In the present study, four different coatings were formulated by the incorporation of cardanol derivatives (5 wt.%) into a diacrylate formulation (Table 1). These four formulations were placed on steel substrates with a bar coater. The first coating called reference coating, was made up of only the base formulation with a 50:50 weight ratio mixture of tripropyleneglycol diacrylate and 1,6-hexanediol diacrylate and no cardanol additives. The second coating (coating A) contained unmodified cardanol as a free molecule less able to photocrosslink with the diacrylates of the base formulation. The third coating (coating B) contained ethoxy cardanol methacrylate (CM), able to photo-crosslink. The last coating (coating C) contained phosphonic ethoxy cardanol methacrylate (CMP), able to photo-crosslink using UV curing. Table 1 shows the properties of the four types of UV-cured coatings produced. All of the coatings were characterized by FTIR and water contact angle

measurements. As shown in Figure S5, the typical absorption bands of acrylate monomer at 812 cm^{-1} ($\delta_{\text{C}=\text{C}}$)³⁷ and at 1643 cm^{-1} ($\nu_{\text{C}=\text{C}}$)⁴² are assigned to C=O stretching, C=C vibration and =CH alkene twisting absorptions. After the acrylate formulations were exposed to UV light between 1 and 3 rounds, a significant reduction in the signals of the absorption peaks at 1643 cm^{-1} and 812 cm^{-1} was observed, confirming the occurrence of photopolymerization. In the other side, the alkyl chain of cardanol double bonds characterized by the out-of-plane bending ($\delta_{\text{C}=\text{H}}$) still be present at 720 cm^{-1} after the UV curing. These coatings had an average thickness of $30\text{ }\mu\text{m}$.

Table 1: Characteristics of the UV-cured functional coatings.

Coating Type	Reference	Coating A	Coating B	Coating C
	Base formulation	 Diacrylates (mixture of tripropylene glycol diacrylate and 1,6-hexanediol diacrylate)	 Base formulation + 	 Base formulation + 
Thickness* (μm)	30 ± 3	30 ± 2	31 ± 3	28 ± 1
Water contact angle ($^\circ$)	45	70	72	52
Adhesion test classification	0B	0B	1B	5B

* Thickness analyzed by POSiTest DFT accompanied by standard error of the mean ($SE = \sigma/\sqrt{n}$); average of 9 points

The properties of the coatings containing cardanol or cardanol derivatives were compared with the base formulation. Adhesion test and water contact angle measurements were performed to assess the contributions of the different additives. The formulations containing 5 wt.% CMP showed total effectiveness in the adhesion test (5B classification, 0% of coating area removed), whereas the base reference coating had a 0B classification, meaning that greater than 65% of the coating area was removed. The coatings containing free cardanol or

non-phosphonated cardanol methacrylate also performed poorly in the adhesion test, with a classification of 0B and 1B (35-65% of the coating area removed), respectively. Measurements of the water contact angles highlighted the contribution of the unmodified fatty chain of cardanol to the increased hydrophobicity of the coating. The contact angle increased from 45° to 70-72° with the addition of 5 wt.% of free cardanol or CM, while the contact angle was only 52° for the CMP-containing coating. This may be explained because the phosphonic acid groups, which are mainly located on C7 or C8 of the C15 chain, counterbalance the hydrophobic effect of the side alkyl chain. In addition, phosphonic acids are known to migrate at the interface between polymer film and metal substrate.⁴³ This could also explain the WCA values observed for coating C. There were no significant differences, in terms of contact angle or adhesion efficiency, between the resulting coatings prepared from the addition of 5 wt.% free cardanol or from CM.

Preparation and characterization of latex coatings

Two latex-based coatings, one containing CMP and MMA, the other containing CM and MMA, were synthesized using aqueous miniemulsion polymerization to compare the effect of the phosphonic acid groups in latex coatings. Latex properties are summarized in Table 2. The first latex containing a mixture of CMP and MMA at a mass ratio of 50:50 was prepared at 10 wt.% solids content. Initial attempts to synthesize this P(CMP_{50-co}-MMA₅₀) latex by conventional emulsion polymerization proved unsuccessful as the resulting latex was not colloidal stable. A brown polymer was obtained among a white latex, suggesting that a CMP-rich polymer phase separated out of the PMMA latex. Initial experiments with cardanol-derived monomer suggests that it might be due to the surfmer behavior of the CMP monomer in water, modifying its diffusion across the aqueous phase. Indeed, surfmers (surface active monomers) are molecules that combine the functionalities of surface activity, polymerizability and reactive groups, so that a surfmer acts as both surfactant and monomer⁴⁴. The phosphonic acid function is highly polar⁴⁵ and so the CMP monomer should be less hydrophobic than the CM monomer. A copolymerization in toluene was also carried out with CMP and MMA targeting a 50:50 mass ratio to determine if CMP and MMA were able to copolymerize. The conversion vs. time data (Figure S6) show that the two monomers copolymerized but that CMP polymerized much faster (53% monomer conversion) than

MMA (23% monomer conversion) at the end of 6 hours. This may have led to the formation of CMP-rich polymer particles with insufficient stabilization, which eventually caused colloidal instability and separation in the latex. Miniemulsion polymerization was implemented to increase the stability of the particles in the latex. This eliminates the nucleation step as well as the mass transfer step of CMP through the aqueous phase as the monomer droplets formed by sonication at the beginning of the reaction are the actual sites of polymerization. A 10 wt.% solids, a P(CMP₅₀-co-MMA₅₀) latex was successfully synthesized using SDS as surfactant, hexadecane as hydrophobe, and V-65 as hydrophobic radical initiator. A redox initiating system consisting of ascorbic acid and *tert*-butylperoxybenzoate at a molar ratio of oxidant:reductant of 2:1 was also used at the end of the polymerization to ensure quantitative monomer conversions (by redox reaction with *tert*-butylperoxybenzoate, incorporated into the latex at the beginning of the reaction). In our previous work²⁹ on the miniemulsion copolymerization of CM and MMA the use of this redox system was successful to bring the polymerization to complete monomer conversions. Nevertheless, here, a colloidally stable, light brown P(CMP₅₀-co-MMA₅₀) latex with a particle diameter of 148 nm was obtained using the miniemulsion polymerization protocol. The second latex containing a homogeneous mixture of CM and MMA was prepared using a of 50:50 mass ratio and a solids content of 20 wt.%. A colloidally stable, white P(CM₅₀-co-MMA₅₀) latex with a particle diameter of 98 nm was obtained.

Table 2: Summary of polymer latex properties.

Polymer*	Particle diameter		pH after polymerization
	D _i (nm)	PDI	
P(CMP ₅₀ -co-MMA ₅₀)	148	0.23	1.6
P(CM ₅₀ -co-MMA ₅₀)	98	0.01	1.6

*weight fraction

To avoid the immediate corrosion of the steel plates upon application of the latexes (due to the direct contact of acidic water with steel), the latexes were neutralized with sodium bicarbonate to a pH of 5.2 prior to application with a bar coater. The two latexes were then applied onto steel plates and dried in an oven at 80°C for 8 h before characterization of the coating properties (Table 3). Due to the low solids content of the latexes (10 wt.% and 20 wt.% for P(CMP₅₀-co-MMA₅₀) and P(CM₅₀-co-MMA₅₀), respectively), an even layer of coating on the steel plates was difficult to obtain. The coating thickness was quite uneven

across the surface, averaging to 10 μm thick for P(CMP₅₀-co-MMA₅₀) and 15 μm thick for P(CM₅₀-co-MMA₅₀). Adhesion test and hydrophobicity measurements were performed nonetheless. The adhesive effects of the phosphonic acid group of CMP were evidenced by comparison of the two latex coatings. Adhesion tests performed on both plates in zones of similar thickness showed that the phosphonic latex coating had a slightly lower percentage of coating area removed (47% vs. 58%), although both coatings were classed as 1B. However, similarly to what was observed in the case of the UV-cured coatings, the use of CMP led to a less hydrophobic coating with the water contact angle decreasing from 77 ° for P(CM₅₀-co-MMA₅₀) to only 33 ° for P(CMP₅₀-co-MMA₅₀). In literature,⁴⁶ a PMMA coating had a WCA around to 60°. This relatively low WCA suggests that this CMP-containing coating could have weaker barrier properties compared to the CM-based coating.

Table 3: Characteristics of latex functional coatings

Coating Type	P(CMP ₅₀ -co-MMA ₅₀)	P(CM ₅₀ -co-MMA ₅₀)
Thickness* (μm)	10 \pm 2	15 \pm 2
Water contact angle [#] (°)	28 \pm 4	75 \pm 3
Adhesion test classification	1B	1B

*thickness analyzed by BykoTest on zones for adhesion test, [#]WCA was not influenced by difference of surfactant ratio.

Application of cardanol-derived monomers in protective coatings

The use of CM in coatings resulted in an increased hydrophobicity caused by the cardanol C15 alkyl chain. This enhanced hydrophobicity should also translate into improved barrier properties. The use of CMP on the other hand resulted in improved adhesion properties due to the strong interaction of the phosphonic acid moieties and the metal substrate. However, the additional presence of these phosphonic acid groups also led to reduced hydrophobicity of the resulting coating, maybe due to the migration of the modified cardanol at the coating/metal interface (which in turn lead to a coating/air interface mainly composed of PMMA chains). Alternatively, considering the large amount of CMP contained in this latex coating, the inferior hydrophobicity could be also caused by the higher hydrophilic character of CMP compared to CM.

This trade-off between higher hydrophobicity and better adhesion may be improved perhaps by combining both latexes into a coating (CM-based latex for its hydrophobic

character and CMP-based latex for its adhesion performance) or by adjusting the proportions of phosphonic and non-phosphonic cardanol into a latex formulation. Another possible improvement could be to target core-shell structures (using a seeded emulsion polymerization technique) so that CMP are located at the surface of the polymer particles. This could increase the interaction between phosphonic acid groups and the steel plate and minimize the required CMP content.

Conclusion

The synthesis of a new biobased phosphorylated monomer from cardanol for use in protective coatings is presented. Phosphonic ethoxy cardanol methacrylate (CMP) was synthesized from cardanol via hydroxyethylation, followed by 1) phosphorylation using UV radical addition of dimethyl phosphite onto the unsaturations present in the C15 aliphatic chain of cardanol, 2) methacrylation of the hydroxyl ethoxy group, and 3) cleavage of the phosphonate ester groups to generate the targeted phosphonic acid moieties. The effects of cardanol derivatives on the performance of protective coatings were evaluated in UV-cured coatings as well as in latex coatings. In UV-cured coatings, increased hydrophobic properties were observed in formulations containing free cardanol or CM compared to the base diacrylate coating. The incorporation of phosphonic acid groups onto cardanol significantly increased the adhesion effectiveness of the coating. No significant differences were observed in terms of contact angle or adhesion effectiveness between the coatings containing free cardanol or CM. For latex coatings, colloiddally stable 10 wt.% solids P(CMP₅₀-co-MMA₅₀) and 20 wt.% solids P(CM₅₀-co-MMA₅₀) latexes were successfully synthesized by miniemulsion copolymerization in water. An additional redox initiation system (*tert*-butylperoxybenzoate/ascorbic acid) was used near the end of the 6 h copolymerization to ensure quantitative monomer conversions. The contributions of the fatty chain of CM and of the phosphonic acid groups of CMP were similar to those observed in UV-cured coatings. A higher adhesion effectiveness was observed in CMP-based coatings compared CM-based coatings. The much higher water contact angle observed for CM-based coatings compared to the CMP-based coatings showed that the hydrophobic effect of the side alkyl chain is counter-balanced by the hydrophilicity of the phosphonic acid groups and/or by migration of the CMP monomer toward the metal–coating interface. To the best of our knowledge, the synthesis of a phosphorylated cardanol-based methacrylate and its use in protective

coatings has not been previously reported. This novel biobased adhesion-promoting monomer is a valuable first foray in the design and preparation of protective coatings featuring both higher performance and lower environmental impact.

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