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Latex coatings containing antifeedants: Formulation, characterization, and application for protection of conifer seedlings against pine weevil feeding

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ABSTRACT

Latex-based coatings for protection of tree seedlings against pest insect feeding are evaluated with respect to surface-, mechanical-, and release properties and antifeedant activity. The latex dispersion Eudragit copolymer (EC) was used to form the coatings, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and *cis*-dihydropinidine (Alk) as antifeedants, and a thickener and a alkylglucoside based nonionic surfactant were used as additives to optimize the release- and mechanical properties of coatings. Coating characterization was performed with respect to surface morphology (atomic force microscopy, AFM) and surface wetting (contact angle), as well as to mechanical (tensile stress- and tensile strain at break) properties. Surface smoothness and wettability as well as elasticity increased with addition of the surfactant. The optimized coatings were found to be elastic and water resistant at 3–6 wt.% of BHT and 3 wt.% of surfactant. BHT was released into SDS/water at very low rates. Several formulations of BHT and Alk were efficient in preventing the feeding on conifer bark by a pine insect, *Hylobius abietis* both in laboratory (no-choice) and in field (3 months) tests.

1. Introduction

Latex is generally an aqueous suspension of a naturally occurring hydrocarbon polymer or an emulsion of synthetic rubber or plastic obtained by polymerization [1–3]. Coatings based on latex dispersion have many advantages over conventional coating systems based on organic solvents. For example, due to the aqueous nature, these materials are not flammable and/or toxic, thus no explosion hazard or environmental contamination is expected [4]. Latex is widely used in surface coatings, paints, textiles, furniture, packaging, construction, pharmacy, etc. [1,4–6]. Pharmaceutical industries use them to formulate controlled release drug delivery systems in order to protect dosage forms from moisture and UV exposure [5,6]. In recent years the use of latex coatings in controlled release pesticide formulations has received much attention from the research community [7]. The idea is to develop a formulation that contains a pesticide that will be released at constant rate during a long period of time. In this work we have used such formulations trying to solve the problem of protecting conifer seedlings against insect feeding.

Insect feeding is a great problem to forestry, since the economical losses can be substantial. For instance, the pine weevil, *Hylobius abietis*, – a pest insect feeding on young conifer tree transplants – can kill up to 80% of young pine and spruce seedlings in 1 year [8]. Certain chemical compounds, called antifeedants, may be used as tree protectants. They must, on the one hand, effectively prevent the insect from feeding on the tree seedlings, and, on the other hand, not be hazardous to mammals or to the ecosystem in general in which it acts. During recent years significant efforts have been made for protection of seedlings using both chemical [8–16] and mechanical [8,10] approaches. Earlier we have shown both 2,6-di-*tert*-butyl-4-methylphenol, well known as butylated hydroxytoluene (BHT), and a naturally occurring piperidine alkaloid, (D,L)-*cis*-dihydropinidine, to have the desired antifeedant activity [14,16,17]. Nevertheless the necessity for developing more effective and environmentally friendly antifeedant formulations has become obvious for a long-lasting seedling protection to be obtained. The coatings must meet the following requirements: (i) to be elastic enough to withstand the rigors of the tensile and compressive forces that occur during growth of the seedling; (ii) to secure as low release rate as possible of the active compound still retaining the biological activity; (iii) to be insoluble in water (rain) to minimize coating loss during at least 2 years which is the time needed before the seedling becomes strong enough to withstand insect attacks.

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Mechanical properties are important characteristics of coatings since the coating may carry out multiple tasks in the field. First it should be stable over time, meaning that it should not be too brittle. It should also be highly elastic in order to elongate as the tree seedling grows with time (the aim of these coating is to last ca. 2 years). A coating may also, through its toughness, offer mechanical protection against the insects biting. The elastic modulus, describing the rigidity of the polymer coating and relative elongation, and tensile strength, describing the ductility of the film are important indicators in these respects [5].

The main aim of this work was to develop a new and novel latex formulation containing antifeedant(s) to be used in the field. To achieve this we characterized the coatings and tested the new formulations for their antifeedant activity. Four main components are used in the formulation: Eudragit copolymer, latex dispersion, a thickener, a surfactant, and an antifeedant compound, mainly BHT. A series of formulations containing varying amounts of BHT and surfactant were prepared. The surface properties (morphology by AFM and contact angle) and the mechanical properties of the formed coatings such as tensile stress and tensile strain at stretching where then investigated. The release of BHT from the different coatings into water was also studied. Finally, the antifeedant activities of the different formulations/coatings on conifer seedlings against *H. abietis* feeding were determined.

2. Experimental

2.1. Materials

2,6-Di-*tert*-butyl-4-methylphenol (BHT) was supplied by Acros, USA. Eudragit, a poly(ethylacrylat-methylmethacrylate) aqueous dispersion 30%, was donated by Donsmark Process Technology A/S, Denmark. The product contains 1.5 wt.% of a stabilizer. The thickener, a hydrophobic modified ethylhydroxyethylcellulose, and the surfactant (S), an alkylglucoside based nonionic surfactant were kind gifts from Akzo Nobel Surface Chemistry AB, Sweden. Analytical grade ethanol and sodium dodecylsulphate (SDS) were purchased from Merck, Germany. All materials were used as received, without further purification. Milli-Q water was used throughout the experiments. The alkaloid, (D,L)-*cis*-dihydropinidine (Alk), was synthesized in accordance with a procedure described by Eriksson et al. [16,18].

2.2. Preparation of dispersions

All formulations were water-based and contained a film-forming latex dispersion in water, a thickener and an ethanol phase carrying the BHT which is poorly soluble in water. Surfactant was added to some formulations, with the aim to improve the mechanical properties of the coatings and to optimize the release rate of BHT.

A series of formulations – Eudragit copolymer (EC), Eudragit + BHT (EC + B) and Eudragit + BHT + surfactant (EC + B + S) – were prepared and are presented in Table 1. The main steps of the formulation procedure are: a warm ethanol solution of BHT (13%, 27%, 30% and 36%, w/w) was added drop-wise to a stirred mixture of thickener, surfactant and Eudragit copolymer dispersion. The mixture was left overnight at continuous stirring in order for BHT to be well dispersed in the mixture and to properly dissolve the polymer. The final concentrations of BHT in the dried formulations were 4.5%, 6%, 9% and 12% (w/w). The surfactant concentration was varied between 3% and 12% (w/w). In each series the concentration of surfactant and BHT was varied, whereas the concentrations of Eudragit copolymer and thickener were kept constant.

Table 1
Composition of the dispersions (%, w/w)

Components	EC	EC + S	EC + B	EC + B + S
Ethanol solution of BHT	–	–	33.3[a]	33.3[a]
Eudragit copolymer	99.2	93.2	67.7	59.9
Thickener	0.8	0.8	0.8	0.8
Surfactant	–	6.0	–	6.0

[a] Four different ethanol stock solutions were used: 13%, 27%, 30%, and 36% (w/w). The final BHT concentration in the dry formulation was 4.5%, 6%, 9%, and 12%. EC = Eudragit copolymer, B = BHT (antifeedant), S = surfactant.

2.3. Preparation of coatings

The preparation of the latex coatings was performed according to the standard procedure of latex film formation [1,2]. Pure Eudragit copolymer forms a transparent elastic coating. However, the addition of BHT and/or surfactant during the formulation process affects the transparency of the film: the higher the content of an additive, the more opaque the resulting film. It was also noted that when the BHT content was increased the film adopted a more rough structure. These results were obtained simply by inspection of the coatings. For mechanical measurements, surface morphology studies, dynamic angle tests and release tests the dispersions were put on glass slides and carefully handled by a 4-sided paint applicator to form a layer of uniform and well defined thickness. The formulations were allowed to dry at ambient conditions. After evaporation of the solvent during 1 day the coatings were considered fully formed. Coatings of 170 μm thickness were used for mechanical measurements, whereas in contact angle measurements and release studies the thickness was about 50 μm. The thickness of coatings for surface morphology studies was 20 μm. For the bioassay tests the formulations were applied either by a simple brush on the pine seedlings (field) or by dipping the twigs (laboratory) and dried at ambient conditions during at least 24 h. The length and weight of the coated layer on each seedling were approx. 10 cm and 0.5 g, respectively (field). The pine twigs were fully covered with the coating (laboratory).

2.4. Coating morphology

The surface morphology was studied on a NanoScope III atomic force microscope (Digital Instruments, Santa Barbara, CA, USA) fitted with a NanoScope IIIA controller and a Dimension 3000 large sample type G scanner. The coatings were analyzed in tapping mode with standard silicon tips. The roughness average (Ra) was calculated as the average of surface elevation values relative to a center plane and corrected for tilt in the NanoScope software program.

2.5. Contact angle measurements

The contact angle measurements were performed with a Dynamic Adsorption Tester, DAT 1100, Fibro Systems AB, Sweden. The DAT-instrument consists of a sample stage, a liquid delivery system, a light source (halogen lamp) and a video camera. These are connected to the computer, which determines the contact angle and droplet volume automatically from the registered image. Milli-Q water was used as a test liquid. A water droplet (4.0 μl) was deposed on the sample surface and images of the drop in contact with the surface were taken. The contact angle values were monitored as a function of time; average value of 10 measurements has been used.