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# Influence of surface modified nano silica on alkyd binder before and after accelerated weathering

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ABSTRACT

Introduction of nano fillers in exterior wood coatings is not straight forward. Influence on aging of polymer binder needs to be taken into account along with possible benefits that nano fillers can provide immediately after application. This study shows the influence of two differently modified hydrophobic nano silica on an alkyd binder for exterior wood coatings. One month after application, the highest strength and energy required to break the films was obtained with addition of 3% disilazane modified silica. Changes in tensile properties were accompanied with a small increase in glass transition temperature. However, the highest stability upon accelerated weathering, measured by ATR-IR and DMA, was for nano composites with the highest amount of nano filler. The reasons for the observed changes are discussed together with the appearance of a feature that is possibly a secondary relaxation of alkyd polymer.



## 1. Introduction

Use of nanotechnology is increasing in the wood coating industry. Reinforcement of interior wood coatings presents a clear benefit for parquet lacquers and furniture coatings where mechanical resilience is a very important parameter. In exterior wood coatings nano fillers are presently predominantly used to improve UV protection; although superhydrophobic, self-cleaning coatings or nano based preservatives are likely to be important in the future [1].

Addition of nanofillers in exterior coatings usually impacts mechanical properties. Mechanical properties are typically considered of secondary importance for exterior wood coatings, but their improvements will of course always be viewed as favorable. With a slow change towards biobased materials in the coating industry, the limiting constraint can be that they often have weaker mechanical properties compared to conventional materials [2,3]. Manipulation of these properties can become more important in the future. When hard inorganic nano particles are added into a polymer matrix an increase in stiffness is often seen. However, of much higher importance is the flexibility and toughness of exterior wood coating as it needs to follow the movement of wood without cracking for a prolonged period of several years [4]. Dimensional changes of wood due to absorption/desorption of water are a cause of constant stress on the wood coating and could lead to fatigue failure. The difference in thermal expansion coefficient of wood and coating is another cause of stress on the protective coating [5–8]. As polymer glass transition temperature ($T_g$) affects the flexibility a lot, influence of coating constituents on polymer $T_g$ and on the $T_g$ stability over time will be of utmost importance.

Due to the large surface area of the nanofillers increased stiffness and restrictions in polymer chain mobility should occur with the addition of nanofiller, and polymer $T_g$ usually increases to a certain extent. However, when tests were performed after

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weathering on exterior coatings, it was seen that nano particles can have different effect on $T_g$. Both an increased or decreased stability of $T_g$ over time, compared to the nano filler free controls, was seen [9–11]. This means that the polymer-particle interface and the interactions between the polymer and filler have an influence on the $T_g$. The stability of $T_g$ over time can potentially also be affected by the presence of surface active compounds which are often used as dispersing aids for preparation of nano composites.

To the best of our knowledge there are no studies from this perspective with the use of nano silica in wood coatings. Nano silica was shown to improve mechanical properties of interior wood coatings like abrasion and scratch resistance [12,13] or stiffness and tensile strength [14,15]. A well-known effect of nano silica as a toughening agent for brittle polymers like epoxides [16] can become important with stiffening of exterior wood coating over time. A long oil alkyd was chosen as a binder in this study. The basic structure of an alkyd polymer is given in Fig. 1. Alkyds have for a long time been one of the first choices as binders in exterior wood coatings due to their high flexibility, very good penetration into the wood and pigment wetting [17]. Even solvent based alkyd coatings still have a large market share in wood coating industry [18].

In the current investigation, silica particles with different surface chemistries were investigated to determine the effect of a hydrophobic surface coating as well as a reactive particle surface of intermediate polarity. A hydrophobic, hexamethyl disilazane (HMDS) treated nano silica that should have good compatibility with alkyd polymer was used. In recent time and probably even more in the future, water based coatings are increasingly represented, especially in the do-it-yourself part of the market that has a large share in exterior wood coatings. For this reason, it is important to know if the nano filler behaves in the same manner in both solvent and water borne formulations. Tests with low amount of nano filler, that typically provides best results in respect to nanocomposites, were performed in both solvent and water borne formulations. We have also chemically modified hydrophilic nano silica with tall oil fatty acids. This modification increases the compatibility and interactions with the alkyd polymer, and also allows us to study the effect of crosslinking the nano filler with the polymer matrix. Results from one month after coating application and after accelerated weathering are reported and discussed.

## 2. Materials and methods

### 2.1. Chemical compounds

A 100% solid long oil alkyd polymer (60% oil length, acid number = 7) typically used for exterior wood coatings was obtained from PPG Architectural Coatings EMEA, Dyrup A/S together with siccatives (for solvent and water borne coatings), white spirit, industrial emulsifiers, defoamer and tall oil fatty acids (TOFA). The majority of the TOFA sample comprised of the 9,12-octadecadienoic acid (C18:2) and 9-octadecenoic acid (C18:1), which accounted for approximately 48 wt% and 33 wt% of the whole mixture, respectively. All other chemicals were at analytical grade and were used as bought from Sigma Aldrich.

### 2.2. Nano silica filler

Hexamethyl disilazane treated nano silica (further abbreviated as S1) in powder form (20 nm particle size) was used as obtained from Fluorochem Ltd. 7 nm glycidoxypropyl modified colloidal nano silica (S2) commercially known as Bindzil CC 301 was obtained from PPG Architectural Coatings EMEA, Dyrup A/S and this silica was further modified with TOFA. Model structures of different silica used are shown in Fig. 2.

### 2.3. Nano silica modification with TOFA

#### 2.3.1. Preparation of TOFAoyl chloride

TOFA (71.21 g, 0.25 mol) was transferred into a one necked flask and dried using an excess amount of dry toluene and a rotary evaporator. A magnetic bar is then added to the reaction mass and the temperature was reduced to 0 °C using an ice and salt bath. Oxalyl chloride (141.37 g, 1.11 mol) was then transferred dropwise into the reaction mass followed by 10 drops of dimethylformamide (DMF). A condenser was fitted onto the system and connected to a nitrogen supply. Reaction mass was then heated to 80 °C for 3.5 h, whereafter the product was isolated by evaporation of the excess reagents. The product was used without further purification.

#### 2.3.2. TOFA grafted silica

The S2 silica to be modified was provided as a dispersion in water, and subsequent lyophilization was carried out to yield a dried sample at mild conditions. The dried S2 (29.28 g) and a magnetic bar was added to a one necked flask followed by adding of dichloromethane. In a separate Erlenmeyer flask 4-dimethylaminopyridine (DMAP, 3.28 g, 0.03 mol) was dissolved with a small amount of dichloromethane and then mixed with triethylamine (52.93 g, 0.52 mol) to make a clear solution. This solution was then added to the flask and the reaction mass was cooled to below 0 °C using an ice and salt bath. TOFAoyl chloride (76.16 g, 0.25 mol) was diluted with dichloromethane and then added drop wise to the reaction mass. The reaction was then carried out at room temperature under nitrogen overnight. The reaction was stopped and diluted with dichloromethane and the resulting dispersion was filtered and dried *in vacuo* at room temperature, to yield the TOFA modified silica (mS2) (Fig. 2b).

### 2.4. Preparation of the coatings

Nano silica was added into the alkyd polymer and dispersed with the use of SpeedMixer DAC 150.1 FVZ-K. Mixing time was 1 min at 1000 rpm and then 3min at 3000 rpm for 3 wt% of nano silica (S1 and mS2). For 8 wt% of S1, the mixing time was 1 min at

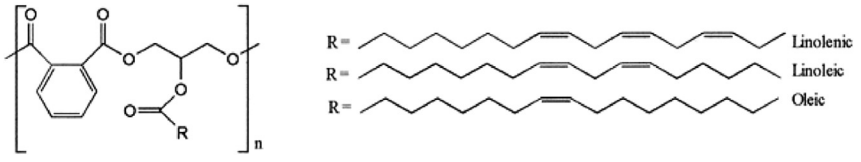


**Fig. 1.** Alkyd structure (Reproduced with permission from Ref. [19]).