



# Mechanical characteristics of alkyd binder reinforced by surface modified colloidal nano silica

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## ARTICLE INFO

### Article history:

Received 23 June 2015

Received in revised form

30 September 2015

Accepted 12 October 2015

Available online 28 October 2015

### Keywords:

Alkyd

Nanocomposites

Surface modification

Colloidal silica

Wood coatings

## ABSTRACT

Performance and longevity of wood as a building material is dependent on the appropriate protection for the desired application. Alkyd based coatings have been in use for decades in order to protect wood. This study reports the influence of two differently modified colloidal nano silica on static and dynamic mechanical properties on a water-borne alkyd binder. An important aspect was to utilize Raman spectroscopy to ensure that all the composites are tested at the same state of cure. Increases of storage modulus and glass transition temperature are reported together with changes in tensile properties. The tensile specimens were observed using SEM to obtain information on failure modes for the pure polymer and nano composites and difference in roughness of fracture surfaces is discussed. A beta relaxation of the alkyd binder was also found and was not hindered by the presence of nanoparticles.

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## 1. Introduction

Wood can be used as building material with characteristics that make it suitable for a wide range of applications. Its performance is dependent on the appropriate protection for the desired application [1]. Wood is most often protected with coatings that prolong service life for both indoor and outdoor uses. Coatings protect wood from environmental influences or damage from mechanical or chemical origin [2,3]. Esthetics can also be tuned with the use of coatings by obtaining the desired color or level of gloss.

Alkyds have been in use for decades in order to protect wood. Traditionally alkyds are used as solutes in organic solvents and wood coatings based on this technology still have around 50% of market share in Western Europe [4]. In other parts of the world, the market share of these alkyd coatings is likely higher. Logical successors of this technology that were developed are water-reducible alkyds and alkyd emulsions. Water reducible alkyds are synthesized as rather polar resins with high acid number. They are first dissolved in water soluble organic solvents and further diluted with water. Alkyd emulsions are made from low acid number alkyds

that cannot be mixed with water and are therefore emulsified with the use of surface active compounds. Mutual characteristic for all alkyds is that the curing reaction is through autoxidation into a limited cross-linked network.

The expansion of nanotechnology in coatings in the past decade or two first started with reinforcement of polymer binders. In wood coatings, introduction of nano size fillers led to changes in hardness, tensile properties, abrasion, scratch resistance, etc. [5]. The nano size of these fillers and thereby their large surface area increases the amount of interface between polymer and filler. In a nano composite, particle–polymer interactions present in the interface thus become an important factor in terms of performance [6]. However with this enormous surface area the free energy of these nano fillers is also high and there is a tendency of the nano particles to agglomerate reducing the high interfacial area and resulting in poor dispersion. To obtain proper dispersion and compatibility with the polymer matrix nano fillers are typically surface modified [7].

The shape of nanomaterials can be different and among spherical particles, inorganic oxides like SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are commonly used because of their high hardness [8]. Platelets such as nanoclays [9] and nanofibers such as cellulose are also in use [10,11]. Surprisingly we have found very little research literature on composites of pure alkyds with nano silica or other spherical nano fillers from a point of view of mechanical characteristics. The

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closest comparison would perhaps be alkyd based polyurethanes where Rodriguez et al. [12] have seen improvements in wear resistance when hydrophobic trimethylsilane modified silica was used. When hydrophilic silica is added into a polyurethane the improvements result from hydrogen bonding [13] though the amount of sites available for hydrogen bonding is substantially higher for polyurethanes compared to typical long oil alkyds. Kurt et al. [14] did demonstrate a decrease in surface hardness of a water reducible alkyd with the addition of non-modified colloidal nano silica. They explained it by increased elasticity of the composite due to hydrogen bonding of alkyd with flexible Si–O bonds on the surface of colloidal silica. However, their observation might as well result from the influence of nano silica on the curing rate.

A water reducible alkyd is different from an externally emulsified type that was used in the present study since it is synthesized with a high amount of polar end groups which are potential sites for hydrogen bonding. Raman spectroscopy has been used in the past to follow the curing of alkyd coatings both for bulk samples [15,16] and at different film thickness depths [17,18]. Raman spectroscopy has been used in the present study to ensure that mechanical properties of samples with different amount of nanoparticles are tested at the same state of cure. This ensures that the impact of nanoparticles is not entangled with that of the (varying) state of cure.

In this study, two differently surface modified colloidal nano silicas have been incorporated into an alkyd binder, typically used in exterior wood coatings, and the mechanical properties of these composites were studied. Small amounts of up to 5% (by weight) of spherical nano filler were used as loadings in this range usually provide the best dispersion, and also have commercial feasibility as the wood coating market is in a low price range zone. Both modifications keep the silica stable in water while providing steric stabilization so that the silica can now be stable at typical pH range (around 8) of water based coatings without the use of additional surfactants. One of silica modifications was very hydrophilic (glycidoxypropyltrimethoxysilane) while the other, also hydrophilic, had a possibility to covalently bind with the alkyd during curing (methacrylamidotrimethoxysilane). In general, the introduction of covalent interactions between nanofiller and polymer matrix is a common method to significantly improve compatibility and stress transfer during loading.

## 2. Materials and methods

An alkyd binder with oil length of 60% (60 g of fatty acid on 100 g of alkyd), externally emulsified with a combination of non-ionic and anionic surfactants to 50% solids in water was obtained from PPG Architectural Coatings EMEA, Dyrup A/S together with an iron based siccative and two different colloidal nano silicas. Both nano silica have primary particle size of 7 nm and were surface modified with two different silanes ((3-glycidoxypropyl)trimethoxysilane and (methacrylamidopropyl)trimethoxysilane) so that they had glycidoxypropyl (S1 in further text) and methacrylamido (S2) functionalities and were still stable in water. Siccative and one of the colloidal nano silicas were mixed into the alkyd emulsion leading to different weight percent of silica (1–5%) based on the solid alkyd content. The mixtures were applied with a manually operated draw down applicator to a Teflon board to obtain free films after curing. The films were carefully removed from the Teflon boards and cut to appropriate sizes for tests; samples were placed in desiccators filled with silica gel at room temperature and 13–15% relative humidity for 24 h before testing of mechanical properties.

Raman spectroscopy was performed on free films at room temperature by a BWTEK i-Raman EX spectrometer model BTC264P-1064S-512, employing a 450 mW NIR 1064 nm laser light source. The spectral resolution was approximately  $10\text{ cm}^{-1}$  while

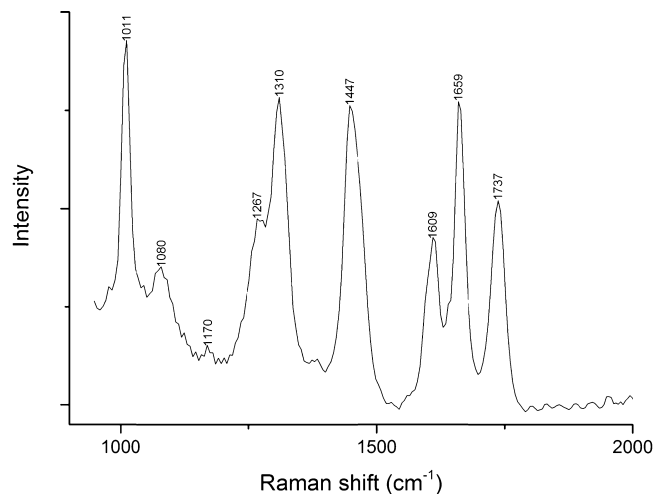


Fig. 1. Raman spectrum of alkyd binder at the start of curing.

integration time was fixed at 5 min. Thickness of tested samples was  $0.070 \pm 0.010$  mm.

Tensile tests were performed following the ASTM D2370 standard and using a Shimadzu testing machine (AGS-X, 20N load cell). Preload of 0.05 N was used and the crosshead speed was 15 mm/min. Gauge length was 25 mm with the sample width of 6.5 mm and thickness  $0.070 \pm 0.010$  mm. At least ten specimens from at least three different free films were prepared and tested for each composition. Tensile strength, elongation at break and modulus of elasticity were calculated automatically using provided software. The fractured surfaces after tensile test were observed using a Scanning Electron Microscope Quanta 200, FEI under high vacuum. The fractured surfaces were coated with gold and operating voltages were 10–15 kV.

Dynamic mechanical analysis (DMA) was performed in tension mode on TA instruments Q800 analyzer. Gauge length was 10 mm, sample width 5.5 mm and thickness  $0.075 \pm 0.005$  mm. Two tests were done for every silica loading level and results are reported as their average. Tests were performed in the temperature range of  $-40$  to  $60^\circ\text{C}$  with temperature increase of  $2^\circ\text{C}$  per minute at a frequency of 1 Hz and strain rate of 0.1%. Some tests were also performed starting from  $-100^\circ\text{C}$  keeping the rest of the settings unchanged. Storage and loss modulus were measured as a function of temperature and glass transition temperature ( $T_g$ ) was assigned from the onset point of storage modulus following the ASTM E1640 standard.

Solid-state NMR experiments were performed on a Bruker Avance 400 spectrometer operating at 400.13 and 100.62 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, using a double-tuned solid-state NMR probe equipped for 4 mm (o.d.) rotors. Recording of  $^{13}\text{C}$  cross-polarization (CP) [19] magic angle spinning (MAS) NMR spectra were carried out at room temperature using a spin-rate of 9 kHz, a contact time of 1.6 ms, a recycle delay of 8 s, 512 scans and an acquisition time of 49.3 ms during which high power TPPM [20]  $^1\text{H}$  decoupling was applied. The spectra were referenced to  $\alpha$ -glycine (external sample) at 176.5 ppm.

## 3. Results and discussion

### 3.1. Raman spectroscopy

It is well documented that nanoparticles can influence the curing of polymeric binders. Rate of curing was seen to both increase and decrease with different nano particles and in different systems [21–25]. Raman spectroscopy was used to follow the curing of

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