Nanofibrillated cellulose in wood coatings: viscoelastic properties of free composite films

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ABSTRACT

Dynamic mechanical analysis (DMA) represents an important method for understanding the mechanical behavior of surface coatings. In this work, transparent composite films of nanofibrillated cellulose (NFC), derived from beech wood pulp, and 10 different commercial polymeric binders, representative binders for wood coatings, were prepared to study the viscoelastic properties of the composite films. DMA in tensile mode was used to determine the glass transition temperature (T_g), the storage and loss modulus and the cross-linking and entanglement density before and after accelerated aging. Additionally, Fourier transform infrared spectroscopy (FTIR) was applied to corroborate the findings of the dynamic mechanical analysis. T_g , moduli, cross-linking and entanglement density of prepared films depended on the initial properties of the neat polymers. The addition of 2.5 wt% NFC to the polymers had no significant influence on T_g and entanglement density, while the reinforcing effect of NFC influenced the moduli of all polymers, as well as the cross-linking density of the alkyds. Accelerated aging by UV radiation at 60 °C strongly affected the viscoelastic properties of neat alkyd polymer and its NFC composite films, while the aging effect was less pronounced for the acrylates. DMA and FTIR findings confirm that unmodified NFC did not adversely change the general aging behavior of the polymers.

Introduction

Waterborne acrylates and alkyds are one of the predominantly applied binders for coatings in outdoor applications to protect the complex, organic and

biodegradable building material wood against UV radiation, humidity and microorganisms [1]. Suitable viscoelastic properties of exterior wood coatings are required to resist stresses, which are mainly induced by swelling and shrinking of the wooden substrate during temperature and humidity

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cycling. Therefore, a high flexibility of exterior coatings is necessary, especially to bridge micro cracks at the wood surface [2].

Thermal analysis comprises a family of measuring techniques which measure a materials response to being heated or cooled, to establish a connection between temperature and specific physical properties of these materials [3]. Dynamic mechanical analysis (DMA) is among others such as differential scanning calorimetry (DSC), temperature-modulated DSC (TMDSC), dielectric analysis (DEA) and thermomechanical analysis (TMA) one of the most popular techniques to determine viscoelastic properties of polymeric materials such as coatings [4]. Samples are subjected to oscillating mechanical stress and strain within the linear viscoelastic region of the polymer, and information on the mechanical stiffness, described by the storage modulus E' and the loss modulus E'' , and the damping or energy dissipation ($\tan \Delta$) are obtained. Additionally, the dynamic glass transition temperature (T_g), which affects the flexibility of a coating, can be determined due to increased molecular motion within the polymer [5, 6]. These parameters determined by DMA are sensitively responding to changes in the polymer network of a coating, e.g., due to varying paint compositions or due to chemical and physical changes of the polymer during weathering [4].

To improve the efficiency of coating systems, nanofibrillated cellulose (NFC) could serve as a new multifunctional organic component for wood surface coatings. NFC is known to mechanically reinforce a variety of polymers and is reported to be used in different coating applications [7–9].

This publication is part of a study about the suitability of NFC in different commercially used, waterborne polymeric binders for wood coating applications. In a first publication, the fibrillation of the cellulose raw material, its characterization and its rheological properties in coating formulations were described [10]. The second publication reported the structural and mechanical properties of the composites assessed by microscopy and tensile tests before and after aging [11]. A third publication presented the effects of NFC on the dispersion and stabilization of zinc oxide (ZnO) nanoparticles in acrylic waterborne wood coatings including tests on coated wood specimens [12].

In accordance to our former publications, this paper presents the impact of NFC on the viscoelastic

properties of acrylic and alkyd polymer binders, as well as the change of these properties due to aging.

Experimental

Materials

A refined fibrous beech wood pulp with 79 wt% cellulose content, 14 wt% hemicelluloses and 0.8 wt% residual lignin (Arbocel[®], J. Rettenmeier & Söhne GmbH&Co. KG, Germany) was chosen as raw material for the production of NFC. Ten different, commercially available polymeric binders, four acrylates, four alkyds, one polyurethane/acrylate hybrid and one polymer dispersion based on ethylene, methacrylic ester and vinylacetate, were chosen to prepare polymer–NFC composites. Table 1 presents these polymer emulsions including their suppliers, their properties as declared by the suppliers and acronyms used in this paper. The additives used and their corresponding suppliers are included in Table 2.

Preparation of NFC

The used NFC was prepared as described before [10]. In brief, the beech wood pulp was diluted with deionized water to give a suspension of 1.5 wt%. After swelling, the pulp was treated in an inline dispersing system (Megatron MT 3000, Kinematica AG, Switzerland), followed by a treatment in a high-pressure homogenizer (Microfluidizer[®], Microfluidics Corporation, USA). The resulting NFC suspension was concentrated by centrifugation for storage at 5 °C. For more details, check Ref. [10].

Preparation of polymer–NFC composite films

Polymer–NFC composite films were prepared using a standard coating formulation based on the suppliers' recommendations (compare Table 2 or supporting information in the appendix).

For a better comparability, a constant polymer solid content of 25 wt% was used in all formulations. A defoamer, to minimize foaming during processing, and a wetting agent for better substrate wetting, a film forming agent for Acr4 and a drying agent for the alkyds were used as essential additives for processing. NFC suspension was added to polymeric

Table 1 Suppliers and types of used aqueous polymer emulsions

Name	Commercial name	Supplier	Polymer and stabilization	Solid content (wt%)
Acr1	Alberdingk AC 2739	Alberdingk Boley GmbH, Germany	Acrylic acid/methacrylic acid co-polymer emulsion, surfactant free, Self-cross-linked	44–46
Acr2	Acronal DS 6288	BASF SE, Germany	Anionic acrylic emulsion	44
Acr3	Mowilith LDM 7416	Celanese, USA	Acrylic acid/methacrylic acid styrene co-polymer, anionic surfactants	49–51
Acr4	NeoCryl XK-98	DSM N.V., Netherlands	Anionic, acrylic copolymer emulsion	44
Alk1	Resydrol AY 586	Cytec Industries Inc., USA	Surfactant free acrylic modified core shell long oil alkyd resin emulsion (58% fatty acids)	45
Alk2	Uradil AZ-516	DSM N.V., Netherlands	Anionic, surfactant free long oil alkyd emulsion (63% tall oil)	59–61
Alk3	75% W'Sol NW 474 + 25% E 150 W	Worlée, Germany	long oil amine and co-solvent free alkyd emulsion (74% linseed oil) + medium oil PU alkyd emulsion (44% linseed oil)	55
Alk4	W'Sol 31C	Worlée, Germany	Anionic, modified linseed oil polymer (90% linseed oil)	45
PU1	80% AC2739 + 20% U5201	Alberdingk Boley GmbH, Germany	Acrylic acid/methacrylic acid co-polymer emulsion + anionic, polyester	44
VAC1	Mowilith LDM 1865	Celanese, USA	Anionic, polymer dispersion based on vinyl acetate, ethylene and methacrylic acid esters	52–54

Table 2 Standard formulations of polymer–NFC suspensions for preparation of polymer–NFC composite films with 2.5 wt% NFC content

Component	Content in suspension (%)						
Binder acronym	Acr1,2	Acr3	Acr4	Alk1,2	Alk3,4	PU1	VAC1
Binder solid content	25	25	25	25	25	25	25
NFC (dry/solid content)	0.64	0.64	0.64	0.64	0.64	0.64	0.64
Defoamer	0.5 ^a	0.5 ^b	0.5 ^b	0.5 ^b	0.5 ^c	0.5 ^a	0.5 ^b
Wetting agent	0.2 ^d	0.2 ^d	0.2 ^d	0.2 ^d	0.2 ^e	0.2 ^d	0.2 ^d
Film forming agent	–	–	2.85 ^f	–	–	–	–
Drying agent	–	–	–	0.25 ^g	0.25 ^g	–	–
Deionized water	73.66	73.66	70.81	73.41	73.41	73.66	73.66
Sum	100	100	100	100	100	100	100

^a TEGO Foamex 822 (Evonik Tego Chemie GmbH, Germany)

^b BYK-028 (BYK Additives & Instruments, Germany)

^c W'Add VP6410 (Worlée, Germany)

^d BYK-348 (BYK Additives & Instruments, Germany)

^e W'Add 340 (Worlée, Germany)

^f Butyl glycol (Alfa Aesar, USA)

^g Octa Soligen Co 7 aqua (OMG Borchers GmbH, Germany)

binders to generate polymer–NFC composites. The composite polymer–NFC films contained 2.5 wt% of NFC relative to the solid polymer. Acrylic–NFC composites were also prepared with different NFC contents. Concentrations were 1, 2.5 and 3.5 wt% of NFC relative to the solid polymer, which corresponds to 0.25, 0.64 and 0.91 wt% NFC in the wet

suspensions. Additionally, reference polymer films, further called neat polymer films, were prepared. Instead of aqueous NFC suspension, water was added to reach the same initial solid content (25%) of the wet suspension.

The polymer emulsions were diluted with the calculated amount of water. Afterward, additives were

added while stirring with a dissolver stirrer. NFC suspension was added, and the whole suspension was stirred for 30 min.

Polymer–NFC composite films were prepared using a bar coater with a 500- μm gap onto a polypropylene (PP) foil. The PP foil was pre-treated with the wetting agent to enable a sufficient spreading of the polymer–NFC suspension.

The bar-coated films with an area of approximately 60×250 mm were dried at constant conditions of 20 °C and 65% RH for at least one day, removed from the foil and stored at the same climate for at least 4 weeks.

Accelerated aging of polymer–NFC composite films

Polymer–NFC films without and with 2.5 wt% NFC were subjected to aging by artificial exposure. One representative acrylate (Acr3) and alkyd (Alk1) were chosen. Free films were prepared as described above and were fixed onto birch plywood covered with white paper as supporting substrate. The prepared specimens were aged in a fluorescent UV-accelerated weathering tester (QUV, Q-Lab, USA) according to ISO 11507. The films were exposed to UV light (UVA-340 lamps) with a peak irradiance set to 0.89 W/m^2 at 340 nm under constant temperature of 60 °C and dry humidity conditions for 24, 48, 96, 168, 240 and 480 h.

Dynamic mechanical analysis (DMA)

Viscoelastic properties of neat polymer and composite films were investigated with a DMA RSA III (TA Instruments, New Castle, USA). The free standing polymer films were assessed via film-tension mode in the temperature range of -20 to $+80$ °C (occasional -40 to $+120$ °C) with a heating rate of 2 °C/min at 1 Hz frequency and 0.1% strain amplitude.

Rectangular-shaped specimens were cut from the free standing films with an overall length of 50 mm and widths of 6 mm. Film thicknesses ranged between 80 and 180 μm with an arithmetic mean of 117 ± 25 μm .

Determination of glass transition temperature

Glass transition temperature (T_g) is, according to ASTM D 4092-01, the approximate midpoint of the temperature range over which the glass transition

takes place. Depending on the technique and the operating conditions, different parameters and terms related to the glass transition are used. Particularly, the glass transition temperature obtained by DMA can be referred to as dynamic T_g .

In this study, the temperature corresponding to the peak value of loss modulus E'' versus temperature curve was taken as the glass transition temperature as recommended in the standard ASTM D 4065-94. Since this temperature typically coincides with the temperature at which storage modulus (E') is declining at the fastest rate [13], this method is a simply applicable and very useful solution. In addition, our measurements confirmed that these data are in good accordance to T_g based on the inflection point of storage modulus E' .

Calculation of cross-linking density

The cross-linking density v_x is an important characteristic of thermoset organic coatings (such as alkyds), which represents the mobility of polymer chains during the physical aging processes. The value of E' in the rubbery plateau region is commonly used to calculate the cross-linking density, since E' at low frequencies corresponds to the equilibrium elastic modulus and depends primarily on the tightness of the network structure.

E' at the rubbery plateau was used to calculate the cross-linking density by applying Eq. (1):

$$v_x = \frac{E'}{3R_{\text{gas}}T} \quad (1)$$

where R_{gas} is the gas constant and T is temperature in Kelvin [14].

Authors are aware that this method is defined for unfilled polymer systems only. Nevertheless, we used the method for the following reasons. In contrast to conventional fillers (e.g., carbon black or silicates), our coating composites consist of two polymer networks (alkyd and cellulose). They can interpenetrate and entangle, and due to their functional groups they are able to link. Especially due to hydrogen bonds and hydrophobic interactions, temporary physical cross-linking of NFC and polymer is possible. Therefore, we think that the calculation of cross-linking density might not give an absolute value but definitely can give some information about the tightness of the network structure and how it changes during aging.

Density of entanglement

The acrylates used in this work are linear molecules that entangle both inter- and intramolecularly when they are sufficiently long. The molecular weight between entanglement nodes M_e is significantly controlled by the chain stiffness and can be calculated from the shear storage modulus G' at the point of inflection using the theory of rubber elasticity [15, 16]:

$$M_e = \frac{\rho R_{\text{gas}} T}{G'} \quad (2)$$

The shear storage modulus G' can be replaced by:

$$G' = \frac{E'}{2(1 + \nu)} \quad (3)$$

where ν (Poisson's ratio) is approximately 0.32 (PMMA at 20 °C) [17].

The restrictions to chain sliding are often modeled as temporary physical cross-linking between polymer chains. Analog to the cross-linking density for thermosets, the density of entanglement can be calculated for non-cross-linked thermoplastics:

$$\nu_e = \frac{\rho N_A}{M_e} \quad (4)$$

where ρ is the mass density and N_A is Avogadro's number. Values of ν_e for the various acrylates are calculated by combining Eqs. (2), (3) and (4).

As the application of this method is restricted to non-cross-linked thermoplastics, there is a conflict when using it for coating composites with NFC. As already mentioned for the cross-linking density, we think that the calculation might not give an absolute entanglement density value but useful information about the tightness of the network structure and how it changes during aging.

Fourier transform infrared spectroscopy (FTIR)

Chemical changes in the neat polymer and the composite films after artificial aging were monitored by FTIR. Spectra were recorded on a Tensor 27 (Bruker, USA) in the range of 4000–500 cm^{-1} with 32 scans per measurement. All recorded spectra were normalized to the reference peak at 1450 cm^{-1} (Acr) and 1466 cm^{-1} (Alk), respectively. CH_2 -bending, which should be unaffected by aging, is assigned to those peaks.

Results and discussion

Viscoelastic properties of NFC–polymer composites before aging

DMA was used to determine the T_g of all tested coating systems. Figure 1 presents the T_g of the neat

Figure 1 T_g of neat polymer and polymer–NFC composite films before accelerated aging (T_g = peak value of E'' versus temperature plot).

polymer films compared to the T_g of the polymer–NFC composites with 2.5 wt% NFC. The addition of 2.5 wt% NFC to the neat polymer had only little influence on the T_g , with no clear trend to increase or decrease. Differences were 2.1 °C in average with a maximal shifting of −7 °C for alkyd Alk1 and −5 °C for Alk2. The slightly reduced T_g of Alk1–3 gives evidence that NFC hampers the cross-linking process of the polymer.

Determination of cross-linking density using DMA

NFC acts as reinforcing agent in the polymer–NFC composite due to its three-dimensional network. The cross-linking densities based on E' at the rubbery plateau increased clearly for all tested binders after addition of 2.5 wt% NFC (Fig. 2). The increase ranged between 157% for the terpolymer VAC1 and 259% for the copolymer Alk3. The slightly decreased T_g after addition of NFC (see Fig. 1) and the almost identical FTIR spectra for the neat polymers and the equivalent NFC–polymer composites (compare Fig. 10) let suppose that the calculated increase of cross-linking reflects the effect of mechanical reinforcement of the polymer by the NFC network due to interpenetration and entanglement. Furthermore, temporary physical cross-linking of NFC and polymer due to hydrogen bonds and hydrophobic interactions seems to additionally restrict the chain mobility, seen in the increased E' at rubbery plateau, while there is no significant covalent chemical cross-linking between polymer and NFC, as verified by FTIR.

Figure 2 Cross-linking density of neat polymer and polymer–NFC composite films before accelerated aging.

Determination of density of entanglement using DMA

The calculation of mechanical entanglement densities based on E' at T_g for all acrylates and the acrylate/polyester showed no clear trend (Fig. 3). The differences between the pure polymers and NFC polymer composites were less than 25% and partly in the range of the standard deviation. Thus, the addition of 2.5 wt% NFC does not significantly influence the density of entanglement of the acrylates.

Influence of NFC on the viscoelastic properties

Acr3 was chosen as an example for the acrylate binder systems, and it shows the typical characteristics of thermoplastic polymers (Fig. 4). The first decline of E' at increasing temperature up to approximately 40 °C represents the glass transition, while the second decline stands for the softening of the material.

In the glassy state below T_g , the polymer shows a high storage modulus E' due to C–C bonds, which are not able to spin, and due to entanglement knots of the chains that act as cross-linking points. When the temperature reaches the T_g , the storage modulus decreases due to a better flexibility of the polymer segments and a partial slip or release of the entanglements. The addition of 3.5 wt% NFC in maximum does not change this general behavior. The results showed that the incorporation of NFC into an acrylic polymer matrix increases the storage modulus over the complete temperature range, but to different extents. A similar effect was also observed when

Figure 3 Density of entanglement of neat polymer and polymer–NFC composite films before accelerated aging.

Figure 4 Effect of different NFC contents on the storage modulus E' and the loss factor $\tan \Delta$ of Acr3 as representative acrylate.

nanoparticles, nanoclay or pigments were implemented into a polymer matrix [4, 14, 18].

In the glassy region, E' increased to a maximum extent of 20% (at -20°C) for all tested acrylic films with 3.5 wt% NFC. The NFC network constrains the polymer mobility which leads to an increased stiffness of the NFC-acrylate film, especially at higher temperatures. Above T_g , in the rubbery state at about 40°C , the value of E' at least doubled for Acr1, Acr2, Acr3. For Acr4 and PU1, we observed only a small increase of E' , which was less than 15% over the whole tested temperature range.

The addition of NFC to the acrylic binder decreased the loss factor $\tan \Delta$ (Fig. 4). This decrease indicates a restriction of the polymer relaxation caused by the NFC network. This was observed for all tested acrylates. For Acr3, we also observed an increase of the softening point with increasing NFC content, visible in a shift of the second $\tan \Delta$ peak.

Figure 5 Effect of NFC addition on the storage modulus E' and on the loss factor $\tan \Delta$ for Alk2 as representative alkyd.

The softening temperature increased from 76 to 83°C . The other three acrylates, which have a much higher initial softening temperature ($\sim 100^\circ\text{C}$), did not show that effect.

In comparison, the alkyd binder systems showed the typical characteristics of a thermosetting polymer. The addition of NFC influenced the storage modulus of the tested alkyd binder systems in different ways.

The storage modulus below the temperature of $\tan \Delta$ peak decreased for the alkyds Alk1, Alk2 (see Fig. 5) and Alk3 after addition of 2.5 wt% NFC. The reduced storage modulus and the slightly decreased T_g indicate that NFC hampers or delays the cross-linking of the alkyds. At high temperatures, above $\tan \Delta$ peak, NFC-containing films show increased storage moduli compared to the neat polymers. As already mentioned for the acrylates, the influence of NFC on the storage modulus increased at higher temperatures. The NFC network reduces the

movement of the polymer chains, which leads to an increased stiffness of the NFC-alkyd films, even if the chemical cross-linking of the polymer itself might be slightly reduced.

Alkyd Alk4 with 90% linseed oil and the terpolymer VAC1 showed a slightly different behavior. The addition of 2.5 wt% NFC increased the storage modulus over the whole tested temperature range, again more pronounced at higher temperatures. The low softening resistance of Alk4 at temperatures above 40 °C was improved by the addition of NFC.

Above glass transition temperatures, the addition of 2.5 wt% NFC to the alkyd binder caused a decreasing loss factor $\tan \Delta$ (Fig. 5). This restriction of the polymer relaxation caused by the NFC network was observed for all tested alkyds and also for VAC1. Below the glass transition, the differences of the loss factor $\tan \Delta$ for the initial polymer and the NFC-polymer are negligible.

Viscoelastic properties of NFC-polymer composites after aging

Aging experiments were performed on free films of alkyd Alk1 and the four acrylates Acr1-4 by artificial exposure under UV light at 60 °C and dry humidity conditions. It has to be considered that our coating formulations did not contain light stabilizers, which prevent or retard chemical degradation and which are usually included in commercial coating formulations. Therefore, a fast degradation could be expected.

It is well known that aging processes are changing the viscoelastic properties of a polymer. A low value of E' and a high value of $\tan \Delta$ indicate a low inter-facial stress between wood and coating due to the viscous movement of the coating [20]. Furthermore, there exists a correlation between the stability of T_g and the resistance to weathering [20]. Therefore, it is important to know how a certain amount of NFC influences the T_g , E' , E'' and $\tan \Delta$ of a polymer during weathering.

Before aging, the acrylates were stiffer, with mainly higher tensile strength than the alkyds and showed comparable elongations at break [11]. From the literature, it is known that polymers embrittle mainly due to UV radiation which frequently causes increased MOE and tensile strength accompanied by decreased elongation at break [21, 22].

Acrylates

The viscoelastic properties of acrylates were less affected by aging than the alkyd binder. Polymer aging accompanied by continued film formation instead of chemical cross-linking which is induced by UV radiation is a possible explanation. Aging was already described to increase the polymer stiffness, which is a result of different processes, including the evaporation of residual plasticizing solvents and the process of gaining thermodynamic equilibrium in the polymer network by reducing the free volume for polymer chain movements [22, 23].

Figure 6 shows the storage modulus E' and the damping factor $\tan \Delta$ for the four tested acrylates after different exposure time 0, 24, 96, 240 and 480 h. As expected, the self-cross-linked acrylate Acr1 showed nearly no change of the viscoelastic properties during 480 h UV radiation, while for the other, not chemically cross-linked copolymers, a discreet increment of E' and a slightly shift of T_g toward higher temperatures was observed. Solely the pure, not chemically cross-linked acrylate Acr2 showed a clear increase of E' and a significant shift of T_g already after 240 h. Acr 2 samples after 480 h exposure were too brittle for preparation and testing.

Additionally to polymer aging, polymer degradation by oxidative chemical reactions can be induced upon long-term UV radiation, whereby network defects are introduced to the polymer. Photo-oxidative reactions result in new hydroxyl and carbonyl functionalities, seen in FTIR spectra as progressive increment of the O–H stretching ($3100\text{--}3600\text{ cm}^{-1}$) and a broadening of the carbonyl band (1726 cm^{-1}) to lower wavenumbers due to the formation of alcohol/hydroperoxide groups and unsaturated ketones [24]. The acrylate systems Acr2 (Fig. 7) and Acr3 showed some photo-oxidative aging, while the other tested acrylates stayed nearly unchanged up to 480 h (FTIR spectra not shown).

Acrylic polymers are also prone to photo-induced chain scission and macro-radical disproportionation, resulting in terminal double bonds (1638 cm^{-1}). A slight increase of the 1638 cm^{-1} band indicates the beginning of this degradation process for all acrylates (see Fig. 7 for Acr2), except Acr1.

Thermal degradation of acrylate/methacrylate will be initiated by splitting off carbonyl groups, visible as loss of absorption in the carbonyl band at 1726 cm^{-1} . A further thermal degradation would lead to material loss resulting in an absorption loss in the finger print

Figure 6 Effect of accelerated aging on the storage modulus E' and the damping factor $\tan \Delta$; Exposure time 0, 24, 96, 240 and 480 h (arrows indicate the trend from 0 to 480 h of exposure).

region ($750\text{--}1500\text{ cm}^{-1}$) [25]. Because of too low temperatures during the test mode, thermal degradation cannot occur and therefore no change was observed in the FTIR spectra of the tested acrylates.

DMA results and FTIR spectra confirm that the general aging behavior is not influenced by the presence of NFC in the polymers.

Alkyds

Polymer coatings deriving from alkyd emulsions dry due to water evaporation and particle coalescence

followed by chemical cross-linking and curing with the help of drying agents and catalysts, respectively [26]. Therefore, significant changes of viscoelastic properties were expected by reason of the film formation process. During artificial aging, the films are exposed to temperatures around $60\text{ }^{\circ}\text{C}$ and also to UV radiation, which both accelerate and reinitiate the curing and cross-linking process, leading to higher cross-linking densities.

Alkyd polymer films with increased cross-links lead to higher stiffness due to lower polymer network mobility, which is represented by higher E' and

Figure 7 Average FTIR spectra of acrylate Acr2 with 2.5 wt% NFC before and after 240 h of accelerated aging (normalized to reference peak at 1450 cm^{-1}).

Figure 8 Effect of accelerated aging on the storage modulus E' and the damping factor $\tan \Delta$; neat Alk1 (a) and Alk1 with 2.5 wt% NFC (b) after 0, 24, 96, 168, 240 and 480 h of exposure (arrows indicate the trend from 0 to 480 h of exposure).

higher T_g values and by a significant shift of $\tan \Delta$ peak (Fig. 8). After 240 h of UV exposure, the T_g of the alkyd with and without NFC is comparable, but the overall shift was somewhat bigger for the NFC-containing films due to a slightly reduced initial T_g before aging. The storage modulus E' increased during aging, which is caused by chemical cross-linking. The increase was higher for the NFC-containing films. These results let suppose that in addition to the chemical cross-linking of the polymer physical cross-linking between NFC and polymer takes place.

The obtained similar curve progressions in Fig. 8 indicate that the general aging trend of the alkyd films caused by UV radiation and heat was not significantly affected by the presence of NFC. Nevertheless, films with NFC behaved differently. While the aged polymers without NFC appeared more

Figure 9 Cross-linking density of the neat alkyd Alk1 and Alk1-NFC composite films after accelerated aging.

Figure 10 Average FTIR spectra of the alkyd Alk1 before and after 240 h accelerated aging (normalized to reference peak at 1466 cm^{-1}).

brittle and tended to break easier during sample preparation and testing, NFC indicated its capacity, to hamper the crack propagation of the surrounding polymer and therefor to prevent the reinforced polymer films from braking.

The calculated cross-linking densities after accelerated aging (Fig. 9) indicate that the autoxidation of the polymer dominates the aging process up to 96 h. A further exposure results in a reduction of cross-linking densities caused by an advanced state of thermal cracking of hydrocarbons and the formation of free radicals, known as beta scission. The trend is the same for the alkyd with and without NFC.

FTIR spectroscopy reveals the very complex change in the polymer matrix during aging (Fig. 10). The curing of alkyds involves unsaturated fatty acid groups, which are incorporated as esters in a pre-polymer. Through-hardening of alkyds is the result of subsequent reactions of linoleate derivatives whereby double bonds are converted into ether cross-links [27]. A distinct increase in C–O stretching of ether bonds (1156 cm^{-1}) indicates this process. Multiple secondary oxidation reactions are also occurring and leading to different carbonyl moieties that finally oxidize to carboxylic acids [2]. An increase of intensities of the C=O stretching (1724 cm^{-1}), a very broad O–H stretching (centered around 3400 cm^{-1}) and C–O stretching (1228 cm^{-1}) signifies the formation of carboxylic acids. At the same time, a decrease in C–H stretching (2856 and 2928 cm^{-1}) was detected along with an increase in O–H stretching ($3200\text{--}3700\text{ cm}^{-1}$) signifying beta scission.

As discussed before, the spectra of neat alkyd and alkyd with 2.5 wt% NFC are nearly identical before accelerated aging (solid lines in Fig. 10). FTIR spectra confirm that the general aging behavior is comparable for alkyds with and without NFC. However, it seems that less ether bonds occurred in NFC-containing alkyds after 240 h UV radiation, compared to the neat alkyd without NFC. This supports the assumption that NFC hampers or delays the cross-linking of the alkyd, as already seen in the DMA results. At the same time, the O–H bond vibrations are slightly higher for NFC-containing alkyds, which might be a result of additional cellulose oxidative cross-linking and physical cross-linking of NFC and polymer. The calculated cross-linking densities support this assumption (compare Fig. 9).

Conclusions

In this study, composite films from NFC and different acrylic and alkyd polymer emulsions were produced. The viscoelastic properties of the films were investigated before and after accelerated aging (UV radiation at $60\text{ }^{\circ}\text{C}$) using DMA. Data obtained before and after aging were analyzed in order to understand the influence of NFC on the viscoelastic behavior of the polymer films. Following conclusions can be drawn:

- The glass transition temperature T_g of different polymer binders for wood coatings varies widely depending on their curing chemistry and composition. The addition of 2.5 wt% NFC to the neat polymer had only a small influence on the T_g .

- The cross-linking densities of the alkyds and the terpolymer with vinyl acetate, calculated on E' at the rubbery plateau, increased clearly after addition of 2.5 wt% NFC. The slightly reduced T_g after addition of NFC and the almost identical FTIR spectra for the neat polymers and the equivalent NFC-polymer composites let suppose that the calculated increase of cross-linking reflects the effect of mechanical reinforcement by NFC network and the physical cross-linking of NFC and polymer.
- NFC hampers or delays the cross-linking of the alkyds during film formation, which is confirmed by a reduced storage modulus in the glassy state. At higher temperatures, above tan Delta peak, the mechanical reinforcing effect of NFC leads to increased storage moduli compared to the neat polymers.
- The entanglement densities of all acrylates and the acrylate/polyester changed only marginally after addition of 2.5 wt% NFC, with no clear trend of increase or decrease.
- The incorporation of NFC into the acrylic polymer matrix increased the storage modulus over the complete temperature range, but to different extents. The NFC network constrains the polymer and reduces the movement of the polymer chains, which leads to an increased stiffness of the NFC-acrylate film, especially at higher temperatures. The decrease of the loss factor tan Delta indicates a restriction of the polymer relaxation also caused by the NFC network and possible physical cross-linking between NFC and polymer.
- DMA results and FTIR spectra confirmed that the presence of unmodified NFC did not adversely influence the general aging trend of the tested polymers. Moreover, the impact of aging on the viscoelastic properties of the alkyds was much higher than the effect of NFC addition.
- However, after accelerated aging, the NFC-containing films were easier to handle during sample preparation and testing and were less prone to rupture.

Overall, NFC appears to be applicable in wood coatings, with no adversely effect on the viscoelastic properties. Findings of this study are promising to use NFC in wood coatings to enhance their performance in external use due to the functionalization of NFC with wood protecting agents.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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References

- [1] Bulian F, Graystone JA (2009) Wood coatings—theory and practice, 1st edn. Elsevier Science, Amsterdam
- [2] Nikolic M, Nguyen HD, Daugaard AE, Loef D, Mortensen K, Barsberg S, Sanadi AR (2016) Influence of surface modified nano silica on alkyd binder before and after accelerated weathering. *Polym Degrad Stab* 126:134–143
- [3] Menczel JD, Prime RB (2009) Thermal analysis of polymers. Wiley, New York
- [4] Schlesing W, Buhk M, Osterhold M (2004) Dynamic mechanical analysis in coatings industry. *Prog Org Coat* 49:197–208
- [5] Koleske JV (2012) Paint and coating testing manual. ASTM International, West Conshohocken
- [6] Menard KP (2008) Dynamic mechanical analysis: a practical introduction, 2nd edn. CRC Press, Boca Raton
- [7] Dufresne A (2012) Nanocellulose, from nature to high performance tailored materials. Walter de Gruyter, Berlin
- [8] Lavoine N, Desloges I, Bras J (2014) Microfibrillated cellulose coatings as new release systems for active packaging. *Carbohydr Polym* 103:528–537
- [9] Vardanyan V, Poaty B, Chauve G, Landry V, Galstian T, Riedl B (2014) Mechanical properties of UV-waterborne varnishes reinforced by cellulose nanocrystals. *J Coat Technol Res* 11:841–852
- [10] Grüneberger F, Künniger T, Zimmermann T, Arnold M (2014) Rheology of nanofibrillated cellulose/acrylate systems for coating applications. *Cellulose* 21:1313–1326

- [11] Grüneberger F, Künigler T, Zimmermann T, Arnold M (2014) Nanofibrillated cellulose in wood coatings: mechanical properties of free composite films. *J Mater Sci* 49:6437–6448. doi:[10.1007/s10853-014-8373-2](https://doi.org/10.1007/s10853-014-8373-2)
- [12] Grüneberger F, Künigler T, Huch A, Zimmermann T (2015) Nanofibrillated cellulose in wood coatings: dispersion and stabilization of ZnO as UV absorber. *Prog Org Coat* 87:112–121
- [13] Sepe MP (1997) Thermal analysis of polymers. Rapra Review Report No. 95, vol 8, no 11. Rapra Technology Ltd, Shrewsbury, p 26
- [14] Mitra S, Ahire A, Mallik BP (2014) Investigation of accelerated aging behaviour of high performance industrial coatings by dynamic mechanical analysis. *Prog Org Coat* 77:1816–1825
- [15] Whitten PG, Brown HR (2007) Polymer entanglement density and its influence on interfacial friction. *Phys Rev E* 76:026101
- [16] Sanden MVD, Meijer HEH, Tervoort TA (1992) Deformation and toughness of polymeric systems: 2. Influence of entanglement density. *Polymer* 34:2961–2970
- [17] Baur E, Brinkmann S, Osswald T, Schmachtenberg E (2007) Saechtling Kunststoff Taschenbuch. Carl Hanser Verlag GmbH & Co. KG, Munich
- [18] Hosur M, Chowdhury F, Gebremedhin O, Jeelani S (2008) Recent advances on the effect of nanoclay on the properties of epoxies and fiber reinforced polymer composites. In: *Advances in Heterogeneous Material Mechanics 2008 - Proceedings of the 2nd International Conference on Heterogeneous Material Mechanics, ICHMM 2008*, pp 159–163
- [19] Bulian F, Matellon A, Melchior A, Menotti D, Tolazzi M, Spagna A, Tanelli M (2011) Using DMA and UV–Vis spectroscopy to predict the performance of wood coatings in outdoor use. *Surf Coat Int* 94:177–180
- [20] Bergamasco D, Bulian F, Melchior A, Menotti D, Tirelli P, Tolazzi M (2011) DMA analysis to predict the performance of waterborne coatings. *J Therm Anal Calorim* 103:65–68
- [21] Nichols M (2002) Anticipating paint cracking: the application of fracture mechanics to the study of paint weathering. *J Coat Technol* 74:39–46
- [22] Skaja A, Croll S, Fernando D (2006) Mechanical property changes and degradation during accelerated weathering of polyester-urethane coatings. *JCT Res* 3:41–51
- [23] Cangialosi D, Boucher VM, Alegria A, Colmenero J (2013) Physical aging in polymers and polymer nanocomposites: recent results and open questions. *Soft Matter* 9:8619–8630
- [24] Melchiorre Di Crescenzo M, Zendri E, Sánchez-Pons M, Fuster-López L, Yusá-Marco DJ (2014) The use of waterborne paints in contemporary murals: comparing the stability of vinyl, acrylic and styrene-acrylic formulations to outdoor weathering conditions. *Polym Degrad Stab* 107:285–293
- [25] Súske E (2005) Charakteristische Eigenschaften laserdeponierter poly(methyl-methacrylat)-Filme. Mathematisch-Naturwissenschaftliche Fakultät, Georg-August-Universität, Göttingen
- [26] Hofland A (1997) Making paint from alkyd emulsions. In: Glass JE (ed) *Technology for waterborne coatings*. American Chemical Society, Washington DC, pp 183–195
- [27] Muizebelt WJ, Hubert JC, Venderbosch RAM (1994) Mechanistic study of drying of alkyd resins using ethyl linoleate as a model substance. *Prog Org Coat* 24:263–279