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INFLUENCE OF WOOD EXTRACTS ON THE UV CURING OF ACRYLATE COATINGS

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ABSTRACT

The effect of wood extracts on the kinetics of UV curing of an urethane diacrylate was studied by real-time FTIR spectroscopy. Whereas extracts from rose wood (*Dalbergia latifolia*) inhibit the reaction, curing is not significantly affected by extracts from teak wood (*Tectona grandis*). Data of the pendulum hardness of the coatings confirm these results. Moreover, the radical scavenging capacity of the extracts was determined relative to benzoquinone by a radiation-chemical method.

Key Words: Photopolymerization; Acrylates; Radical scavengers; Inhibitors; Quinones; Real-time FTIR spectroscopy; Wood extracts; Pendulum hardness; UV curing

INTRODUCTION

Application of ultraviolet (UV) radiation curing technology for wood finishing has grown rapidly over the past 25 years,[1–3] and is expected to grow further in the future. Although considerable scientific work has been carried out on the chemistry and technology of UV curable systems, very

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little information is available on the influence of the wood characteristics on the properties and durability of UV-cured coatings on wood substrates.

Wood is a biological material and a wide variation both within the species and between species occurs. The properties of wood that vary greatly from species to species are wood density, grain characteristics, texture, presence of early and late wood, presence of heartwood and sapwood, presence of extractable substances like resins, fats, and oils etc. All these physical and chemical parameters of wood may have an effect on the properties of the surface coatings.

UV-curable formulations are increasingly used for the pre-finishing of solid wood, wood panels and furniture components, for example as filler-sealer coats, opaque base coats and top coats. Such coatings have relative low shrinkage, show an attractive appearance, and can be cured very fast. These processing advantages are the main reasons for the extensive use of UV coatings in the wood finishing industry.[4]

However, chemical substances such as wood extracts can considerably influence the curing behavior of the coatings. For example, the extracts from the Dalbergia species (*Dalbergia latifolia*) are known[5] to affect the curing of coatings from unsaturated polyester resins. Such interference of the extracts with the UV curing process may lead to

(1) insufficient surface cure leading to tacky surfaces.
(2) inadequate through cure. Through cure plays an important role for the adhesion between various coating layers and the adhesion of the coating to the substrate.
(3) poor mechanical and processing properties of the coatings such as hardness or sandability.

Therefore, studies have been carried out to ascertain how wood extracts influence the curing of UV curable coating systems. In a previous paper[6] we reported on the influence of extracts from *Acacia spp*. on the curing behavior of cationically curable coating formulations. The present work deals with the study of the effect of extracts from teak (*Tectona grandis*) and rose wood (*Dalbergia latifolia*) on the radical curing of an urethane acrylate formulation. Real-time FTIR spectroscopy was used to study their influence on the kinetics of the curing process. Moreover, pendulum hardness was determined to probe their effect on mechanical properties.

EXPERIMENTAL

Materials

Teak and Rose Wood Extracts

Extracts were obtained by Soxhlet extraction with methanol from 100 g of oven dry teak and rose wood meal. The weight of the extracts were 5.5 g from teak wood and 8.4 g from rose wood. A 5% solution of teak wood extract and a 10% solution of rose wood extract (both in HDDA) were used.

Acrylates

Formulations were prepared from an aliphatic urethane diacrylate (Ebecryl 4858) and a bisphenol A epoxy diacrylate (Ebecryl 600), respectively. Hexanediol diacrylate (HDDA) and tripropylene glycol diacrylate (TPGDA) were used as reactive diluents. All acrylates were obtained from UCB Chemicals. Benzophenone and Irgacure 184 (Ciba) were used as photoinitiators.

Formulations

Formulation A was prepared for the real-time FTIR experiments:

Ebecryl 4858	100 parts
TPGDA	30 parts
Irgacure 184	3 parts

The concentration of teak or rose wood extract, respectively, was varied between 0.05 to 0.7 parts.

Formulation B was made for the determination of the pendulum hardness:

Ebecryl 600	50 parts
HDDA	45 parts
Benzophenone	5 parts

An amount of 0.3 to 1.2 parts teak or rose wood extract was added.

The formulation was coated on glass plates and cured by three passes through an IST UV irradiator at a web speed of 10 m/min.

Methods

Real-Time FTIR-ATR Spectroscopy

Real-time FTIR spectroscopy was performed by using a Biorad FTS 6000 spectrometer and a single reflection diamond ATR device ("Golden Gate," Graseby Specac). The spectrometer was set to record 95 spectra per second at a spectral resolution of 16 cm^{-1}.

UV irradiation was carried out with an Osram HBO 100 W mercury arc lamp. The light source was equipped with a water filter for blocking infrared radiation and a 313 nm metal interference filter (Andover Corporation). The intensity of the monochromatic UV light in the focus on the surface of the diamond was 50 mW/cm^2. The sample on the diamond was covered by a quartz plate with a depression with a depth of 4 μm in its lower side to set the thickness of the sample. An electronic shutter (Vincent Associates) directly driven by the spectrometer control system serves for precise synchronization between UV irradiation and spectra recording. The experimental setup is described in detail in Ref. 7.

Conversion vs. time curves were calculated from the decay of the absorption band of the $CH{=}CH_2$ twisting vibration at 810 cm^{-1} by integration of the peak areas.

Determination of Pendulum Hardness

The pendulum hardness of the coatings was determined using a Byk-Gardner pendulum hardness tester 5854 operating according to Koenig.

Determination of the Radical Scavenging Properties of Wood Extracts

Aqueous solutions of N_2O-saturated dimethylsulphoxide (DMSO, Aldrich, HPLC grade, 5 vol%) containing various concentrations of wood extracts or 1,4-benzoquinone (Aldrich, purified by fractionating sublimation), respectively, were irradiated by γ-radiation (dose 133 Gy at a rate of 266 Gy/h). The generated methyl radicals abstract hydrogen atoms from DMSO resulting in the formation of methane which was quantified by gas chromatography (GC head space, column Porapak GS-Q 30 m/0.53 mm, FID detector). Its concentration was related to ethane as internal standard which was formed in side reactions.

Water was purified by a Milli-Q (Millipore) generator (18.2 MΩ cm). Nitrous oxide (Linde, medical grade) was used as received.

RESULTS AND DISCUSSION

Exotic woods such as rose or teak wood are used for a long time for the production of veneer to be used in the manufacture of furniture. When such wood materials are covered with acrylate coatings, low molecular substances may migrate from the wood into the coating. In order to study the effect of such substances on the kinetics of UV curing, investigations by real-time FTIR spectroscopy were performed. The substances were extracted from wood and added in a well-defined manner to an acrylate formulation which was then cured by UV light. Conversion was followed by the decay of an absorption band assigned to the acrylic double bonds. The kinetic conversion profiles of the urethane diacrylate formulation (formulation A) containing different amounts of rose or teak wood extract on irradiation with UV light are plotted in Figs. 1 and 2, respectively.

It can be clearly seen that the cure of the acrylate formulation is not significantly affected by the teak wood extract. In contrast, rose wood extract has considerable influence on the UV curing behaviour. In particular, the polymerisation rate strongly decreases with increasing concentration of rose wood extract in the formulation, whereas only little effect on the induction period is observed. After a continuous irradiation of at least 5 seconds, the conversion in all coatings is almost the same. However, when samples are irradiated for much shorter times (as is usually done in the manufacture of coated wood panels), the residual unsaturation in the coatings strongly depends on the amount of rose wood extract.

This will be pointed up by the pendulum hardness of the coatings. It was determined for coatings with a thickness of 60 microns. Results are shown in Fig. 3. It is obvious that the rose wood extract affects the hardness of the UV cured coatings much more than the extract from teak wood. This can be presumably attributed to the lower degree of cure which is achieved in the presence of the rose wood extract.

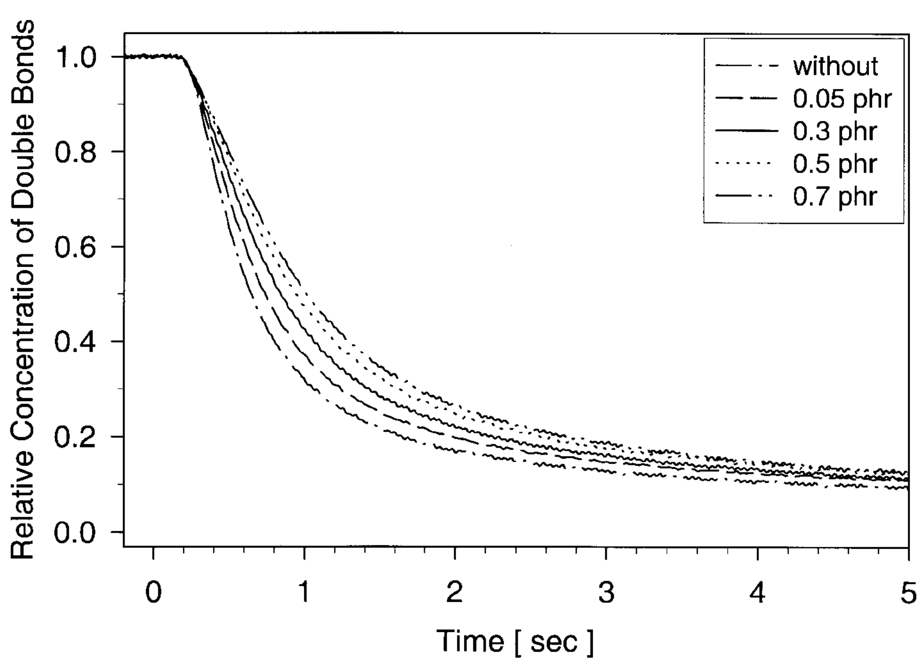


Figure 1. Conversion profiles of the urethane diacrylate formulation A containing various amounts of rose wood extract on irradiation with UV light.

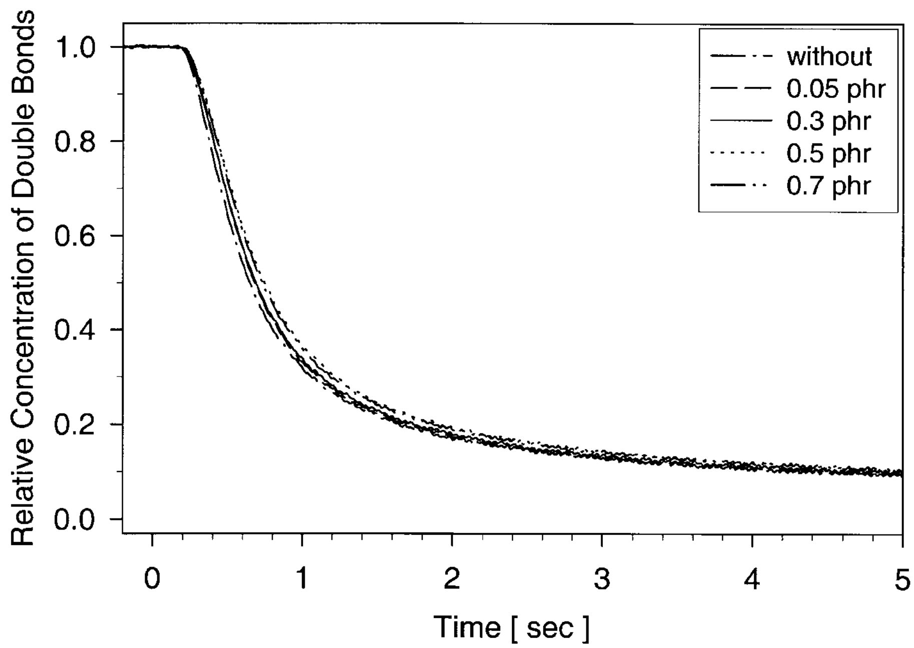
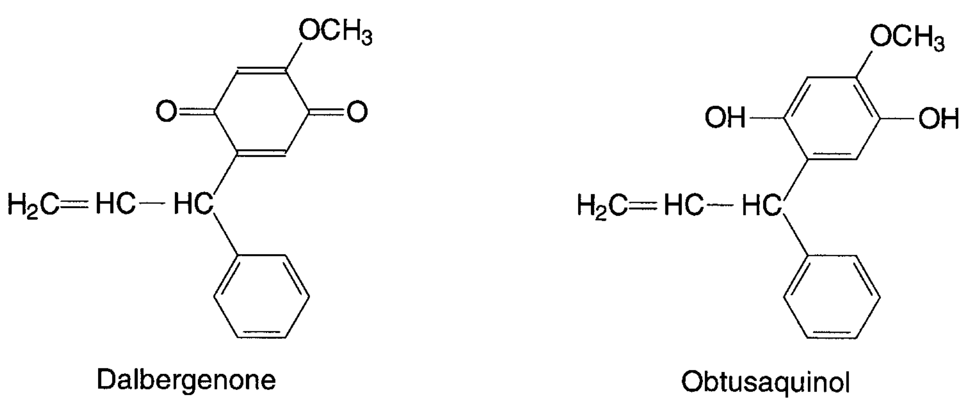


Figure 2. Conversion profiles of the urethane diacrylate formulation A containing various amounts of teak wood extract on irradiation with UV light.

Evidently, the effect of the wood extracts on the curing behavior and the mechanical properties of the coatings does not only depend on their concentration in the acrylate formulation but also on the wood species from which they were extracted, i.e., from the chemical substances which they consist of.

Rose wood is known to contain quinone and hydroquinone derivatives such as dalbergenone and obtusaquinol.[8]



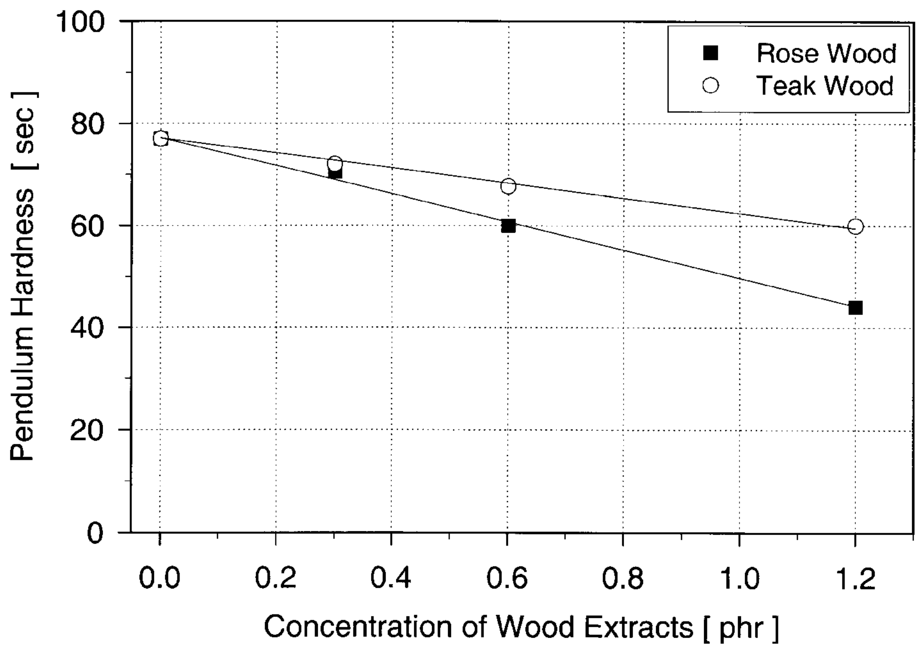
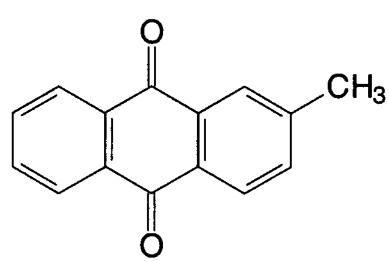


Figure 3. Effect of wood extracts on the pendulum hardness of UV cured coatings made from the epoxy diacrylate formulation B (thickness 60 microns).

It is well known[9] that quinones and hydroquinones act as inhibitors in free radical polymerization. Most commercial acrylates are stabilised for improved storage capability with small amounts of quinones or hydroquinones (in the range of some ppm). Quinones react with active chain radicals and yield product radicals of low reactivity. Hydroquinone and its derivatives inhibit the free radical polymerization in the presence of oxygen due to their oxidation to the corresponding quinones. It is therefore not surprising that the rose wood extract is capable of inhibiting the photocuring of acrylates.

Teak wood is also known to contain a quinone derivative. In its extract, tectoquinone can be detected.



The fact that no significant inhibiting effect of the teak wood extract on the kinetics of UV curing and only minor effect on the hardness of the coatings was observed in difference to the results with the rose wood extract is related to the radical scavenging properties of the both wood extracts. These depend on both the concentration of scavenging substances (such as quinones) in the extracts and on the efficiency of these compounds to scavenge radicals. In general, wood extracts consist mainly of a wide variety of substances such as resins, fats, and oils, etc., which vary from one species to the other. Moreover, they may contain small amounts of quinones and hydroquinones and possibly other (e.g., phenolic) radical scavengers. The exact composition of the extracts and in particular the concentration of scavengers therein is not known.

In order to get a measure for the different degree of inhibition of the radical polymerization by the two extracts used in this study, their total radical scavenging power was determined and compared to that of benzoquinone. Methyl radicals in γ-irradiated aqueous solutions of DMSO can abstract hydrogen from DMSO resulting in the formation of methane.[10] The addition of the wood extracts leads to a scavenging of the methyl radicals by the quinones therein. Consequently, the amount of released methane decreases. Figure 4 shows a fit of the exponential decay of the methane concentration with increasing concentration of rose and teak wood extract as well as benzoquinone, respectively. In fact, the amount of methane formed decreases with increasing scavenger concentration. As expected, the scavenging efficiency of the two extracts is much lower than that of benzoquinone. A solution of 1 g/L teak wood extract has the same scavenging power as 0.005 g/L benzoquinone. However, the equal concentration of rose wood extract corresponds to 0.015 g/L benzoquinone, i.e., its scavenging efficiency is three times higher than that of teak wood. This correlates quite well to the results from RTIR spectroscopy and the mechanical properties.

Complementary, the different properties of the two wood extractives might also be explained by the chemical structure of the various quinones. If benzoquinone derivatives and their corresponding hydroquinones are present in a formulation as in the extract from rose wood, paramagnetic quinhydrones may be formed which are known to be highly efficient radical scavengers. Moreover, benzoquinones are much stronger oxidants ($+104$ mV $Q/Q^{\bullet -}$) than anthraquinones (-390 mV $Q/Q^{\bullet -}$) and thus scavenge also more weakly reducing radicals, which do not react with anthraquinones.[11] Thus, the tectoquinone in the teak wood extract is a much less efficient inhibitor.

CONCLUSION

Real-time FTIR spectroscopy has been proved to be an efficient method to determine the influence of wood extracts on the curing behavior of UV curable coating systems used for the finishing of wood. This study has shown

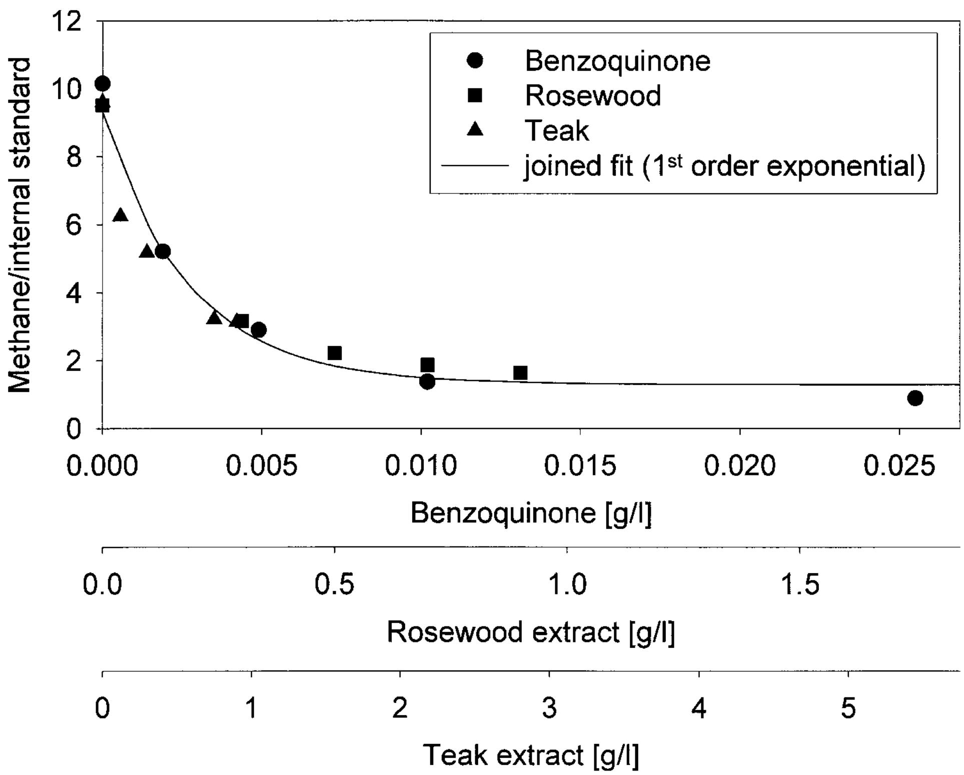


Figure 4. Concentration of released methane relative to an internal standard after radiolysis of 5% aqueous DMSO solutions containing various concentrations of rose or teak wood extract or benzoquinone, respectively.

that rose wood extracts have an adverse effect on the cure of acrylates. The inhibition of the UV curing reaction is due to the presence of quinone and hydroquinone derivatives in the extract from rose wood. In contrast, although quinones are known to be present in the extract from teak wood too, no significant inhibiting effect on the kinetics of UV curing was observed with real-time FTIR spectroscopy. This is related to the lower radical scavenging efficiency of the extract from teak wood which might be due to both the chemical structure and the possibly lower concentration of the quinones therein. Pendulum hardness data of the coatings confirm the results from real-time FTIR spectroscopy.

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