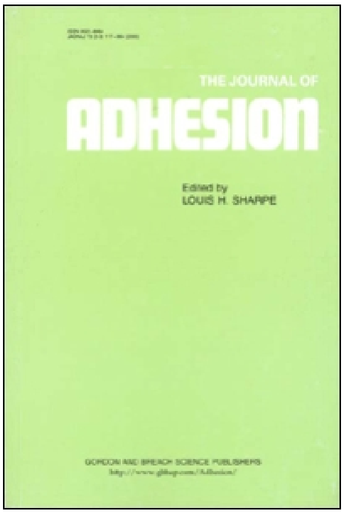

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Evaluation of Water Resistance of Polyurethane Dispersion Coatings by Nuclear Magnetic Resonance Imaging

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Proton nuclear magnetic resonance imaging (NMRI) at 300 MHz is used to evaluate water resistance of polyurethane dispersion coatings. A set of wood rods coated with an uncrosslinked aliphatic polyurethane dispersion, a plasticized poly(vinyl acetate) (PVAc) emulsion and a 5-minute-cure epoxy adhesive, respectively, are immersed in water at 25°C. The water penetration is followed by acquiring cross sectional images from the samples. The same procedure is used at 60°C to compare the performance of multifunctional polyaziridine and polycarbodiimide crosslinkers with the polyurethane dispersion. The signal intensities in the middle of the wood as a function of time show three characteristics for the systems: induction time, absorption rate, and saturation time. The water resistance of the uncrosslinked polyurethane dispersion coating is relatively good. The addition of 2% of the polycarbodiimide crosslinker does not improve the water resistance. However, the same amount of the polyaziridine crosslinker in $300 \pm 50\,\mu m$ thick coatings decreases the water absorption rate by a factor of *ca.* 14. The pot life for the 2% polyaziridine mixture is approximately three days and the coatings made from five-day-old mixture have three times faster water absorption rate relative to the fresh mixtures. The reliability of conventional water resistance tests is also discussed.

KEY WORDS Coatings; NMR imaging; polyaziridine crosslinker; polycarbodiimide crosslinker; polyurethane dispersion; water resistance.

INTRODUCTION

Water resistance of a coating is typically evaluated by immersing the coating in water and observing effects such as color change, loss of adhesion, softening or embrittlement in the film. ASTM standard D870 presents one such procedure, which is widely used, easy and inexpensive. However, there are cases, especially when different types of coatings systems are evaluated, when the results of this kind of test are difficult to interpret and additional information is needed.

Nuclear magnetic resonance imaging (NMRI) has become popular in medical

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science to produce anatomical images from humans and animals.[1-3] Along with the improvements in field strengths, resolution and sensitivity this non-destructive and non-invasive technique has also become useful for chemists and material scientists.[4,5] Applications of this technique has been recently demonstrated, *e.g.* in adhesive studies,[6-11] diffusion studies of polymers[12-15] and with ceramics.[16] NMRI is also an interesting technique to evaluate water resistance properties of coatings and adhesives, since it shows the spatial distribution of water in the sample and observes changes in the materials and coatings with time.

In this paper NMRI is used to evaluate water resistance of polyurethane dispersion coatings. Polyurethane dispersions represent an important group of binders that can replace solvent-based products. However, the key question in most applications involves the water resistance of the films, which can be improved by using crosslinking agents or reactive co-resins.[17] At room temperature only polyaziridine and carbodiimide crosslinkers can be used. Since there were difficulties in interpreting results from conventional tests with these systems, we performed a study using NMRI to get independent information.

EXPERIMENTAL

Samples

Bamboo rods (OD 1.850 ± 0.050 mm) were coated with various binders by dipping. The rods were dipped at 30 minute intervals and dried at room temperature until a coating thickness of 300 ± 50 μm was reached at a specific region of the sample. The binders included a plasticized PVAc homopolymer emulsion (Kestomer V 40 P/Kiilto Oy, Finland; 20% diluted with water), a typical 5-minute epoxy adhesive (Pikaepoksi/Kiilto Oy) and an aliphatic polyurethane dispersion (Neorez R-974/Polyvinyl Chemie Holland bv, Netherlands). The polyurethane dispersion was crosslinked with a multifunctional polyaziridine crosslinker (Crosslinker CX-100/Polyvinyl Chemie Holland bv) and a multifunctional carbodiimide crosslinker (Ucarlnk XL-225 SE/Union Carbide).

The crosslinkers were added to the polyurethane dispersion as follows. 400 mg of the crosslinker was first mixed with 400 mg of water. This mixture was then added to 20.0 g of the dispersion (crosslinker content: 2% on weight, 5% on solids). The crosslinker-dispersion mixtures were then stirred rigorously for 5 minutes, allowed to stand for 20 minutes and stirred for an additional 5 minutes.

Pot lives of the crosslinker-dispersion mixtures were followed by coating a set of rods 1h, 1d, 3d, and 5d after initial mixing of the components.

The coatings were cured at room temperature for two weeks and finally at 50°C for four hours.

Water resistance of the coatings was measured in 15 mm (ID 13 mm) NMR tubes. The rods were cut to a length of 5 cm, sealed with a silicone sealant at the ends and wrapped with Parafilm® except at the slice level ±10 mm. The rods were maintained in the vertical position by inserting both ends in small caps. With the addition of water, the NMR images were acquired at the following times: for 25°C at 1, 2, 4, 6, 8, 10 and 24 h and for 60°C at 0.5, 1, 2, 4, 5, 6, 10, 20, 24 h after immersion. Heated distilled water was used with 0.03% of liquid detergent added to prevent air bubble formation. The temperature was kept constant during the measurements with heated air flow.

NMRI Measurements

All the images were obtained on a Bruker MSL 300 FT-NMR spectrometer, operating at a proton frequency of 300 MHz. The spectrometer is equipped with a MINI and MICRO imaging accessories, but the MICRO imaging probe with 25 mm insert was used for these studies. NMR images were collected on an ASPECT 3000 computer and transferred to a MICROVAX II *via* ETHERNET for further data processing.

The two-dimensional Fourier imaging experiment used a typical Carr–Purcell[18,19] spin-echo pulse sequence with selective 90 degree and non-selective 180 degree pulses with CYCLOPS phase cycling. The selective 90 degree pulse length was 1 ms, while the non-selective 180 degree pulse length was typically 75 μs. The gradient strengths were 9–11 G/cm. Four scans were accumulated to produce images with 256 × 256 pixels from a slice approximately 1 mm thick. A repetition time of 1 s and a spin echo time of 6 ms were used. The accumulation time for one image was approximately 17 min. Images were acquired either at 25°C or at 60°C by using an air heater connected to the probe.

ASTM Standard D 870 Tests

Water resistance of the uncrosslinked plus polyaziridine and polycarbodiimide crosslinked polyurethane films were also tested according to ASTM Standard D 870. The dispersions were applied on glass plates to yield 40 μ thick films. Additionally, the same coatings were studied on wood plates as 200–300 μm thick films. The coatings were dried at 25°C and 55% RH for 48 hours. The dried films were immersed in 60°C water for 8 hours observing changes in the films at 1, 2, 4, and 8 hours after immersion.

RESULTS AND DISCUSSION

Uncrosslinked Polyurethane Coating

To demonstrate the water resistance of the polyurethane dispersion compared with other common binders, a typical fast curing polyamine-epoxy resin system and a plasticized PVAc emulsion were chosen as references of good and poor water resistance systems, respectively. Wood rods with coating thicknesses of 300 ± 50 μm were immersed in 25°C water and NMR images were acquired at 1, 2, 4, 6, 8, 10, and 24 h after immersion. The NMR images of PVAc and polyurethane dispersion coated rods are shown in Figures 1 and 2. The images of

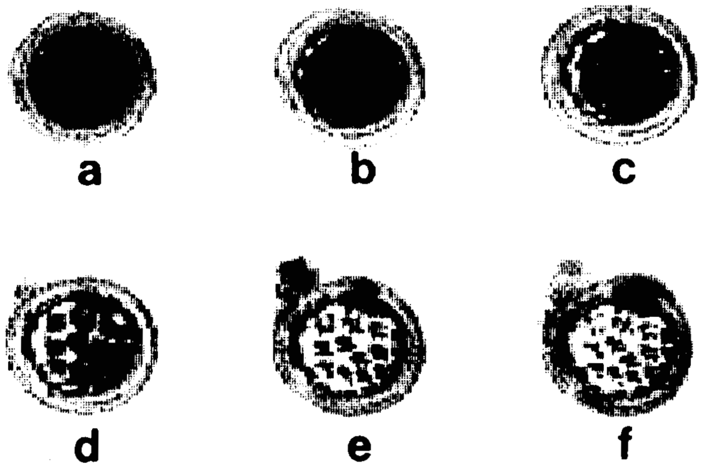

FIGURE 1 Water penetration through the 300 μm thick PVAc coating at 25°C. The NMR images were acquired after following times: (a) 1h, (b) 2h, (c) 4h, (d) 6h, (e) 10h and (f) 24h. White colour represents the highest signal intensity.

epoxy coated sticks did not show any water penetration through the coating within 24 hours.

The PVAc coating shows a very rapid water penetration into the coating (Figure 1a). The coating swells and separate layers of the coating partially delaminate showing poor interfacial adhesion of the layers (Figure 1b–d). After 6 hours of immersion the coating shows deformation (Figure 1d) that continues to grow. While the coating further swells and degrades, the wood reaches saturation at about 10 hours of immersion (Figures 1e–f).

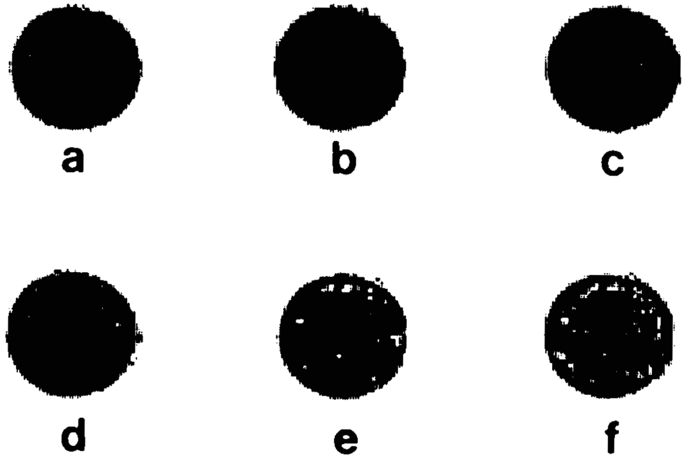

FIGURE 2. Water penetration through the 300 μm thick uncrosslinked polyurethane dispersion coating at 25°C. The NMR images were acquired after following times: (a) 1h, (b) 2h, (c) 4h, (d) 6h, (e) 10h and (f) 24h. White colour represents the highest signal intensity.

The uncrosslinked polyurethane dispersion shows a much better water resistance than the PVAc emulsion (Figure 2). The mechanism of water penetration is also different. The polyurethane coating does not swell appreciably during the 24 hours at 25°C, but rather allows a slow diffusion of water. The differences in the water penetration mechanisms can be explained by at least two factors. First, the PVAc dispersion contains poly(vinyl alcohol) (PVOH) as a protective colloid, which is readily water soluble, allowing the rapid intrusion of water. Secondly, the average particle size of the colloidal polyurethane dispersion is much smaller than that of PVAc dispersion leading to a tighter packing of the dried film.

In Figure 3 the average intensities of 256 pixels in the middle of the wood are plotted as a function of time for the PVAc, polyurethane and epoxy coatings. These graphs as well as those measured at 60°C show that there is an induction time during which water is not detectable in the wood, but may be visible in the coating. Following the induction time, there is an intensity increase in the wood, which can be fit to a linear equation. Finally, a time of saturation can be obtained or estimated from the graphs. These characteristics are summarized in Table I for measurements at 25°C.

Although the factors can describe the water resistance of the coatings, one should understand that the image intensities do not correspond with actual water concentrations. The measured intensity is an average of 256 data points in the image, which covers about 60% of the total wood area. This area included more and less dense wood, but the average reflects well the water absorption or, at the very least, allows differences between the samples and the coatings to be detected. The intensities are dependent on water concentration, but also, on the spin–lattice (T1) and the spin–spin (T2) relaxation times of the protons. The relaxation times of protons in bulk water and water in the coating and wood are different and may vary with time. However, the images and the signal intensities in the wood correlate well with water resistance properties.

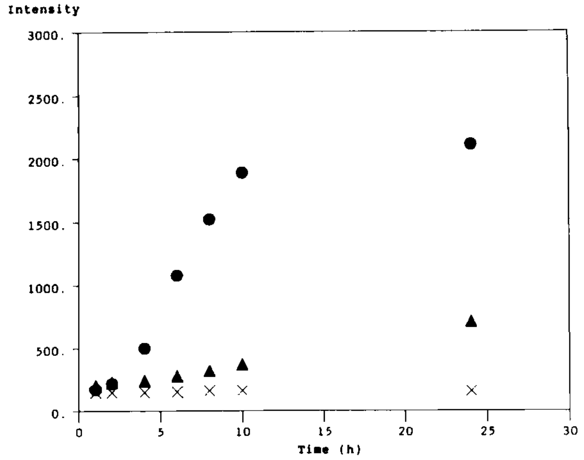

FIGURE 3. The average intensity of 256 pixels in the middle of the wood as a function of time for the PVAc (●), polyurethane (▲) and epoxy coatings (×).

TABLE I
Characteristics of the water absorption through the selected 300 ± 50 μm thick coatings at 25°C

	Epoxy	Polyurethane	PVAc
Induction time (h)	[a]	4–5	1–2
Absorption rate (units/h)	[a]	24 ± 2	220 ± 20
Saturation time (h)	[a]	80[b]	10–11

[a] Not measurable within 24 h.
[b] Extrapolated.

Crosslinked Polyurethane Coatings

To compare the effectiveness of the polyaziridine and polycarbodiimide crosslinkers and to evaluate the pot lives of the dispersion-crosslinker mixtures, sets of wood rods were coated at 1 hour, 1, 3 and 5 days after the mixing of the components. The cured coated rods were immersed into 60°C water, and NMR images were acquired at 0.5, 1, 2, 4, 5, 6, 10, 20 and 24 hours after immersion. Intensities in the middle of the wood were measured and plotted as described above. Table II summarizes the characteristics obtained at 60°C.

The characteristics in Table II show a clear difference in the performance of the two crosslinkers with the polyurethane dispersion used in this study. The coatings made of the polyaziridine crosslinker mixture within three days of mixing have approximately fourteen times slower water absorption rates than the polycarbodiimide systems. The coating made of the five-day-old polyaziridine mixture has a reduced water resistance compared with the fresh mixtures and the absorption rate is approximately three times faster. However, there is no significant variation between the different pot life times of the polycarbodiimide mixtures.

According to these imaging results the use of the polyaziridine crosslinker leads to much better water resistance for the polyurethane dispersion coating. The effectiveness of the polyaziridine crosslinker, however, decreases after three days standing in the mixture, which is due to the self-hydrolysis and loss of the crosslinker. The polycarbodiimide crosslinker, on the other hand, seems to have no effect on the water resistance of the polyurethane dispersion. This is particularly interesting, because the viscosity of the polycarbodiimide mixture clearly increases during the five days iandicating some chemical reaction. Since the very poor performance of the polycarbodiimide crosslinker was unexpected,

TABLE II
Characteristics of the water absorption through the 300 ± 50 μm thick crosslinked polyurethane dispersion coatings at 60°C

	Multifunctional polyaziridine				Multifunctional polycarbodiimide			
Pot life	(1h)	(1d)	(3d)	(5d)	(1h)	(1d)	(3d)	(5d)
Induction time (h)	8–9	8–9	8–9	4–5	<1	<1	<1	<1
Absorption rate	43 ± 4	39 ± 4	43 ± 4	125 ± 10	570 ± 60	560 ± 60	600 ± 60	540 ± 60
Saturation time (h)	65[a]	70[a]	65[a]	24–25	5–6	5–6	5–6	5–6

[a] Extrapolated.

the whole test procedure for the samples representing pot life times of one hour and one day was duplicated. These results were in accordance with those shown in Table II. Additionally, the water absorption of the uncrosslinked polyurethane dispersion coating at 60°C was followed during the first four hours and the rate reflected the same behaviour as the coatings made of the polycarbodiimide mixtures.

Comments about Conventional Tests

The uncrosslinked and crosslinked coatings on glass and wood plates were also evaluated according to ASTM standard D870. During the tests three kinds of changes in the films were observed: total or partial loss of adhesion, whitening and softening of the films. While there were no problems in evaluating the performance of the uncrosslinked and polyaziridine crosslinked films, there were difficulties in interpreting the behaviour of carbodiimide crosslinked film. It resisted whitening almost as well as polyaziridine crosslinked film although, similarly to the uncrosslinked coating it became very soft and lost adhesion to glass. In cases such as this, it is difficult to decide which factor to consider and therefore, additional tests have to be done.

CONCLUSIONS

The polyurethane dispersion coating had a relatively good water resistance. Addition of polyaziridine crosslinker (2%) significantly improved the water resistance leading to *ca.* fourteen times slower water absorption rate. The self-hydrolysis of the polyaziridine crosslinker did not decrease water resistance within three days of standing. However, after five days, the water absorption rate had increased by a factor of three.

The multifunctional polycarbodiimide crosslinker did not improve water resistance of the polyurethane dispersion used in this study.

NMRI was found to be an excellent tool for the water resistance studies, since it shows the actual spatial distribution of water in the sample. Conventional tests that observe secondary effects in the coatings can be in some cases difficult to interpret and even misleading, if additional tests are not performed.

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